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Soil organic matter transformation and stabilization depending on vegetation cover

Doctoral Dissertation Thesis

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Declaration

I declare that the doctoral dissertation thesis "Soil organic matter transformation and stabilization depending on vegetation cover" is my own work that I have conducted under the supervision of my supervisor doc. Ing. Lenka Pavlů, Ph.D. and my co-supervisor RNDr. Václav Tejnecký, Ph.D. All literatures cited in this dissertation thesis are listed in the references.

In Prague on……. 2024

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Ing. Saven Thai

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1. Literature review

1.1. Soil organic matter

The term "soil organic matter" (SOM) refers to various organic components present in the soil, including plant residues, dissolved organic matter, biomass, as well as humus substances (Tinti et al., 2015). SOM plays essential roles in regulating the nutrient cycle, adsorption and desorption of chemical components and especially carbon stabilization (Ohno et al., 2009). SOM, on the other hand, is a mixture of components containing different molecular weights, polarities, and functional groups that could maintain the dynamic of contaminants in the soil (Ukalska-Jaruga et al., 2019). Recently, SOM has been ascribed in a new perception as supramolecular aggregate, which bridges to the functional groups of the molecule and could protect the high quality of organic compounds by the strong bond to metals (Clarholm et al. 2015; Gerke 2018). Metals can form bridges and present in the soil in sufficient amounts to be of quantitative importance including Fe^{3+}, Al^{3+}, and Ca^{2+}. The Mn^{2+} and Fe^{2+} form very weak complexes with organic functional groups. Magnesium is also a less successful bridge builder due to its strength and well-characterized as the second hydration shell. The binding strength between SOM and metals could decrease in the order of $Ca^{2+} < Fe^{3+} < Al^{3+}$ due to the degree of metal hydrolysis, number of bounds to the same molecules and types of the organic functional group involved with Al ions (Clarholm & Skyllberg, 2013).

Furthermore, most of the productive agricultural soil contains organic matter ranging from 1 and 6 %. SOM enhances soil productivity in various ways such as physical, chemical, and biological ways (Magdoff & Es, 2009). In physical way, SOM contributes by enhancing aggregate stability, improving water infiltration and soil aeration, reducing runoff, improving water retention, and reducing the stickiness of clay soil (Branco de Freitas Maia et al., 2013). In chemical ways, SOM helps to improve the soil exchange capacity, enhance the ability of soil to resist pH changes, accelerate soil mineral weathering, and provide essential nutrients more accessible to plants (Branco de Freitas Maia et al., 2013). Regarding the biological way, it serves as nourishment for soil-dwelling organisms, enriches microbial diversity and activity, and increases pore space, which could reduce runoff and improve infiltration (Rumpel & Kögel-Knabner, 2011). Increasing SOM content serves as an essential nutrients source of nitrogen (N), phosphorus (P), and sulphur (S), as documented by Chenu et al. (2015) and Ocio et al. (1991).

Living biomass including microorganisms such as bacteria, fungi, and protozoa contributes to the breakdown of plant residues or detritus and animal waste, transforming them to humus or organic

matter by using carbon as an energy source and nitrogen as a protein source (Kosobucki & Buszewski, 2014). SOM approximately 15% is highly related to the soil microorganisms and other organisms living in the soil (Allison et al., 2007; FAO 2005). Soil organisms such as insects, earthworms, bacteria, and fungi get their energy by decomposing the plant residues or other animal excrements in the soil (Frey 2005). Sometimes the energy which is stored in the plant residues can be used by the organism to create new cells and chemicals. Soil microorganisms, however, can change organic matter by mineralization and recycle nutrients for plant growth. The decomposition of fresh plant residues and manure gives off organic chemical compounds and helps to cling together the soil particles, which improves the soil's physical structures (FAO 2005). Figure 1 shows an example of how the SOM and dissolved organic carbon (DOC) transform into deep soil horizons.
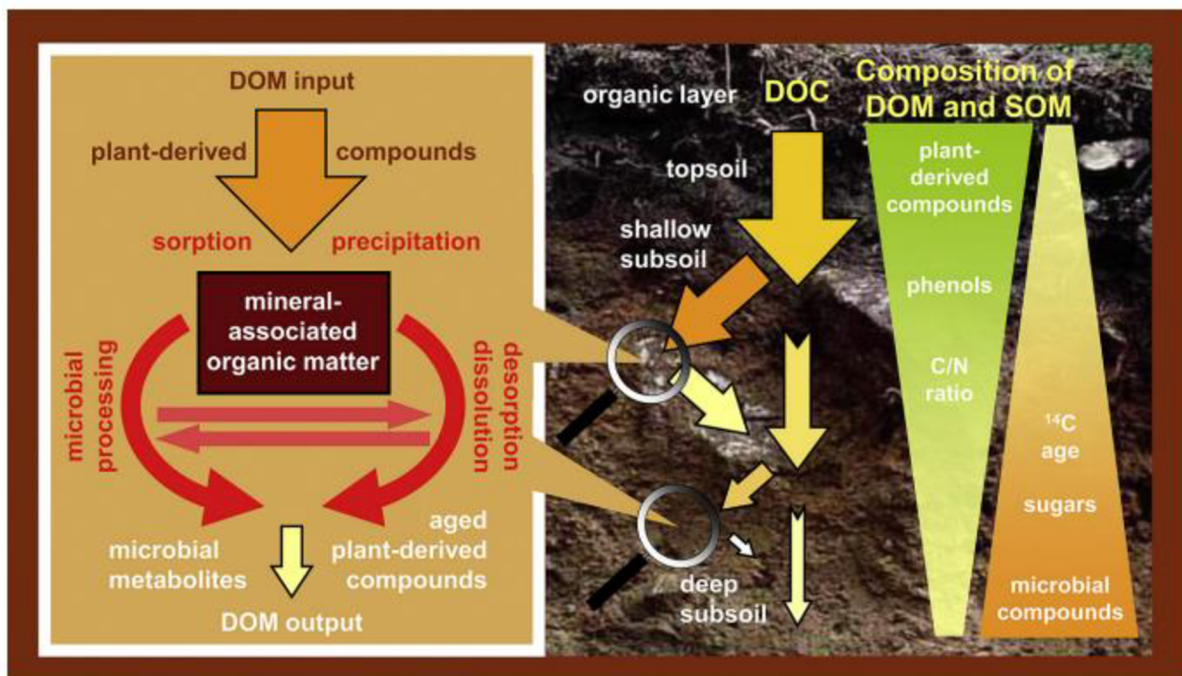
Figure 1. Example of SOM and dissolved organic matter transformation through the soil profile (Kaiser & Kalbitz, 2012).

1.2. Factors affecting soil organic matter

SOM is influenced by numerous factors such as climate, types of vegetation, soil textures, topography, and microorganisms (Lal 2018; Rumpel & Kögel-knabner, 2011; Yuan et al., 2013).

1.2.1. Climate conditions

Climatic factors, including temperature, precipitation, potential evapotranspiration (PET), and a ratio between annual precipitation and PET, cause significant changes in SOM. For instance, a reduction

in the PET-precipitation ratio often leads to an increase in SOM content. In warmer climates, SOM content tends to decline gradually due to rapid decomposition of organic residues (Fang et al., 2005). Additionally, when the climate gets warmer, two things will occur under adequate rainfall conditions: (1) the vegetation is more produced because the growing season is longer and the decomposition rate of organic residues increases due to the more activities and rapidity growth of microorganisms in a longer period of the years, and (2) faster decomposition with warmer temperature become more dominant influences in determining SOM levels (Yan et al., 2017). Climatic conditions such as temperature, rainfall, and seasonal variation have a profound impact on the existence and activities of soil microorganisms and other soil fauna, which, in turn, influence the decomposition rate (Dorji et al., 2014).

Litters decomposition has two simultaneous processes: (1) the association of mineralization and humification of cellulose, lignin, and other compounds through a series of microorganism activities and (2) the leachate of the soluble compound into the soil that carbon and nitrogen are dramatically mineralized (Krishna & Mohan, 2017). These processes take place depending on abiotic factors such as temperature and humidity and biotic factors such as chemical composition and microorganisms. Decomposition is relatively more sensitive to the temperature than the primary production (Fang et al., 2005). A few research confirmed the role of the chemical nature of litter decomposition along with climate conditions (Krishna & Mohan, 2017; Fang et al., 2005: Kader et al., 2017). Additionally, in a very dry climate such as a desert, there is little growth of vegetation and the decomposition rate is also slow because of low amounts of organic inputs and low microorganism community. When there is rain, a rapid decomposition of SOM occurs. Generally, SOM increases as average annual precipitation increases due to water availability for plant growth and production of more organic residues. At the same time, soil with a high rainfall area tends to have slower SOM decomposition than well-aerated soil due to reduced aeration (Magdoff & Es, 2009).

1.2.2. Topography

The topography, such as altitude and slope aspect, significantly affect the organic matter stability, local climate, water content and the translocation of soil organic carbon (SOC) due to erosion and sedimentation (Berhe et al., 2018; Sun et al., 2015; Jakšík et al., 2015, Zádorová et al., 2015). For instance, erosion transports the SOC through runoff over the lands and deposits in the lakes, rivers, or the lower place in the form of sediment. In general, soils at the bottom of the hill are rich in nutrients and organic matter. However, soils on steep slopes or knolls tend to contain lower amounts of organic matter and limits the storage of SOC because the topsoil is continually eroded (Hosseini et al., 2014;

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Dorji et al., 2014). There were few studies reported that the slope and aspect of the SOC stock of a subalpine forest in the Olympic Mountains of Washington state (USA) were relatively higher on the north-eastern slopes, ranging from 43 to 143 g/kg compared to south-western slopes ranging from 27 to 162 g/kg of soil due to the influences of the permafrost dynamics and drainage at the high altitude (Lal 2005; Clarholm & Skyllberg, 2013). Furthermore, a broad landscape with gentle slopes facilitates rapid vertical movement of water through the soil profile, resulting in formation of thick soil profiles with well-developed soil horizons. Conversely, steeply sloping landscapes tend to increase erosion rate and runoff and limit vertical water percolation; therefore, leading to thinner soils and constraints on soil development, as highlighted by Akhtaruzzaman et al. (2014).

1.2.3. Soil texture

The variation in SOM level could be significantly influenced by the soil texture (Turmel et al., 2015). Typically, coarser soils like silt loam and sandy loam tend to have low concentrations of SOM (Clarholm & Skyllberg, 2013). On the other hand, the properties of coarse-textured soil are considered to affect the SOM more than loamy soils (Ellerbrock & Gerke, 2013). Clay and silt soils generally have a higher amount of organic matter than coarse-textured sands and sandy loam soils. The organic matter in sandy soils is typically around 1 %, while in loamy soil ranges from 2 - 3 % of OM, and in clay soil can range up to 4% or even more than 5 % of OM (Magdoff & Es, 2009). Clay and fine-textured particles can combine with organic matter to form tiny aggregates in terms of protecting the organic matter inside against microorganisms and their enzymes (McLauchlan 2006). Chemical bonding substances can also develop between organic matter and clay soil or fine silt to protect molecules from decomposition caused by microorganisms (Nimmo 2005). Fine-textured soil, however, tends to have smaller pores and less oxygen, which can limit the decomposition rate. Therefore, it enhances a higher concentration of OM than coarse soil (Magdoff & Es, 2009). Besides that, clay content may have varying effects on the decomposition of SOM. It is observed that the clay may not significantly influence the SOM decomposition during the early stage of laboratory incubation, but later, it tends to reduce the decomposition rate. In situ, the rate of OM mineralization typically decreases with increased clay content (McLauchlan 2006).

1.2.4. Organisms in the soil

Soil microorganisms play a crucial role in indicating soil fertility and productivity (Esmaeilzadeh & Ahangar, 2014). Plants exert a significant influence on their surroundings through the release of root exudates into the rhizosphere, comprising a wide range of compounds that alter soil chemical and physical properties and facilitate interaction between plants and rhizospheric microorganisms (Macias-Benitez et al., 2020). In figure 2, it shows the soil organisms and their roles in decomposition

of residues. The accumulation and mineralization, as well as the transformation of SOM, are predominantly governed by soil microorganisms (Malý et al., 2014). Vesterdal et al. (2013) stated that the content of SOM decreases through the soil profile due to the microbial activities occurred in the uppermost layer. Microorganisms, however, significantly affect the dynamic of the cations and biogeochemical cycles of the trace metals including plant nutrients. Bacteria and fungi work directly and indirectly with the decomposition processes. Bacteria, in particular, benefit plants by releasing nutrients when they begin to decompose the litter or residues (Rousk et al., 2009; Magdoff & Es, 2009). Many bacteria can dissolve phosphorus for plant uptake and contribute to nitrogen fixation, benefiting both plants and soil improvement. Certain types of bacteria can convert nitrogen gas from the atmosphere into nutrient forms available in the soil, which plants can then absorb as amino acids and protein. On the other hand, nitrogen fixation bacteria can beneficially associate with plants by doing symbiotic relationships, which is suitable for agriculture involving the rhizobia group bacteria that live inside nodules formed on the roots of legumes. Then the bacteria produce nitrogen in a usable form for plants, and in return, plants provide back sugars as energy for bacteria (Wuest & Gollany, 2012). Soil bacteria are also abundant and diverse groups of soil organisms that help regulate ecological processes. Bacteria, including *Bradyrhizobium japonicum, Burkholderia sp, and Mycobacterium sp*, enhance carbon fixation, sequestration, and storage (Yang et al., 2018). The majority of bacteria depend on soil carbon storage to gain energy. For instance, soil bacteria directly decay the SOM and contribute to increasing soil carbon storage in the soil profile. Soil bacteria also indirectly influence soil carbon storage by improving soil aggregation due to the by-products of microbial degradation (Yang et al., 2018). Fungi, on the other hand, can cause various diseases such as damping-off, downy mildew, apple scab, and various types of rotten plant root. However, fungi play a vital role in decomposing the fresh residues or debris and helping other soil microorganisms break down organic residues by softening them. Fungi are also known as the primary decomposer of lignin and can tolerate more acidic soil than bacteria (Baskaran 2017). Low-disturbed soil tends to promote fungal growth and accumulation of organic matter at or near the surface. Fungi and plants have a strong interaction with plant roots, infecting the plant root system and extending hyphae, approximately 1/60 diameter of the plant root (Baskaran 2017). These hyphae can absorb water and nutrients and then feed the plants and exploit the water and nutrients into the small pores of the soil. Hyphae also help plants uptake nutrients and water, and plants provide sugar as energy for fungi by producing it in their leaves and sending it to the root systems. This interaction between fungi and roots is called the mycorrhizal relationship. These hyphae of fungi can also enhance soil aggregation stability by sticking gel, which clings together the mineral and organic particles (Wetterstedt 2010).

Mycorrhizal fungi, which form symbiotic, are highly associated with plants by gaining photo assimilated C and providing the plant nutrient availability (Smith & Read, 2010).
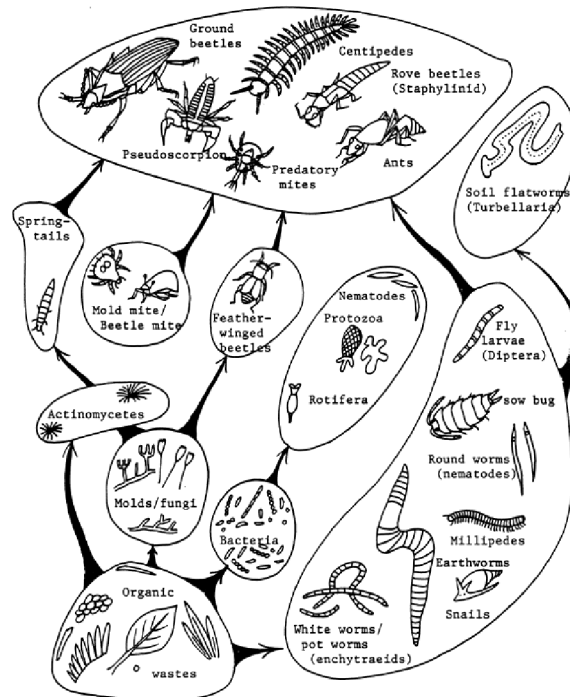
Figure 2. The soil organisms and their roles in decomposition of residues (FAO 1988).

Fungi and bacteria also contribute indirectly to the solubilization processes of trace metals by producing strong acidic or complexing compounds, promoting mineral weathering under anaerobic and aerobic conditions. The microorganisms, however, have difficulties decomposing SOM due to variations in metal binding strength. In situ, SOM decomposition gradually decreases with high Al concentration (Clarholm & Skyllberg, 2013). Hobbie et al. (2007) found that the slow decomposition of SOM can be correlated with the increasing amounts of Fe and Al. However, a high concentration of Ca could be related to retarding the decomposition because of the decreased CO_2 production.

Nematodes and earthworms also play essential roles in regulating soil nutrients and decomposition. For instance, they assist fungi, protozoa, and bacteria in breaking down organic residues (Medina-Sauza et al., 2019; Yadav et al., 2018). On the other hand, earthworm activities serve as biological, physical, and chemical processes, enhancing nutrient movement and soil organic carbon into the deeper soil horizons by loosening the soil profiles (Lemtiri et al., 2014). Earthworms also contribute to soil aggregate stability by releasing the sticky substances from their skin and binding the soil particles with the organic compounds to make good soil structures. Georgia's research indicated a correlation between high earthworm populations and soil rich in organic matter, with a prevalence in

no-tillage compared to conventional tillage soil. Notably, insecticide, pesticide, and fertilization have negative impacts on earthworm growth (Fonte et al., 2010; Magdoff & Es, 2009).

1.2.5. Vegetation cover

The diversity of crops, vegetation, and plants significantly impacts SOM, including the soil organic carbon (Dorji et al., 2014). Figure 3 shows the distribution of SOM in various land uses through the soil profile. Typically, the soil under grassland provides more SOM and distributes deeper than the soil under forestland, followed by cropland due to the deep and extensive root system of the grassland. In the forest, the residues accumulate about 50% of OM on the surface layer, while the subsurface of the mineral layer consists of approximately 3% (Magdoff & Es, 2009). The distribution of SOC in the soil profile continuously varies and is influenced by the subsurface soil inputs of C and the transportation of the carbon into the deeper soil profile (Charro et al., 2017). The decay and formation of SOM can be affected by the interaction of organic residues, soil organisms, and soil conditions in a particular place and can be differed by land covers and land uses (Sun et al., 2015).

In agricultural conditions, tillage is one of the most essential components of the evolution of agricultural production (Khursheed et al., 2019). Tillage can affect soil aggregation, water holding capacity, infiltration, and temperature (Liu et al., 2006). Aeration of soil can also be affected by tillage, which influences water infiltration and decomposition rate (FAO 2017). The more soil tillage, the more breakdown of organic matter occurs in the natural soil aggregate (Liu et al., 2006). Additionally, the topsoil, which consists of high organic matter content, is eroded through rainfall and wind. Some research reported that about 20 % of OM was decreased after five years of cropping corn on clay soil, with a significant loss in the first year (Magdoff & Es, 2009; Liu et al., 2006). However, pesticides, fertilizer, irrigation, and monoculture are also factors affecting the SOM. Yeboah et al. (2016) revealed that conventional tillage causes soil disturbance and reduces organic matter or residues on the soil surface compared to no-tillage soil (Ranjan et al., 2017; Pavlů et al., 2021).

Changes in agricultural practices by reducing tillage, decreasing, or ceasing the fallow period, using winter cover crops, changing from monoculture to crop rotation, or altering soil input to increase the main products are significant alternative methods to increase SOM in the soil (Smith et al., 1998). For instance, grassland and reforestation restoration on the previous crop field can help to reduce the carbon deficit caused by many years of crop cultivation and sequester carbon to the root productivity of plants and crops. Additionally, enhancing ponds and wetlands contributes significantly to carbon

sequestration in the soil profile by minimizing decomposition from microorganisms in the waterlogged region with less oxygen (Magdoff & Es, 2009). Mulching is also widely implemented in horticulture to control weeds, soil moisture, and erosion on steep slopes and preserve the SOM and aggregates. Many researchers reported that the application of organic mulches increased the soil nutrients, soil organic carbon, agricultural productivity, maintained the soil temperature, and reduced water evaporation (Hosseini Bai et al., 2014; Ranjan et al., 2017; and Pavlů et al., 2021).
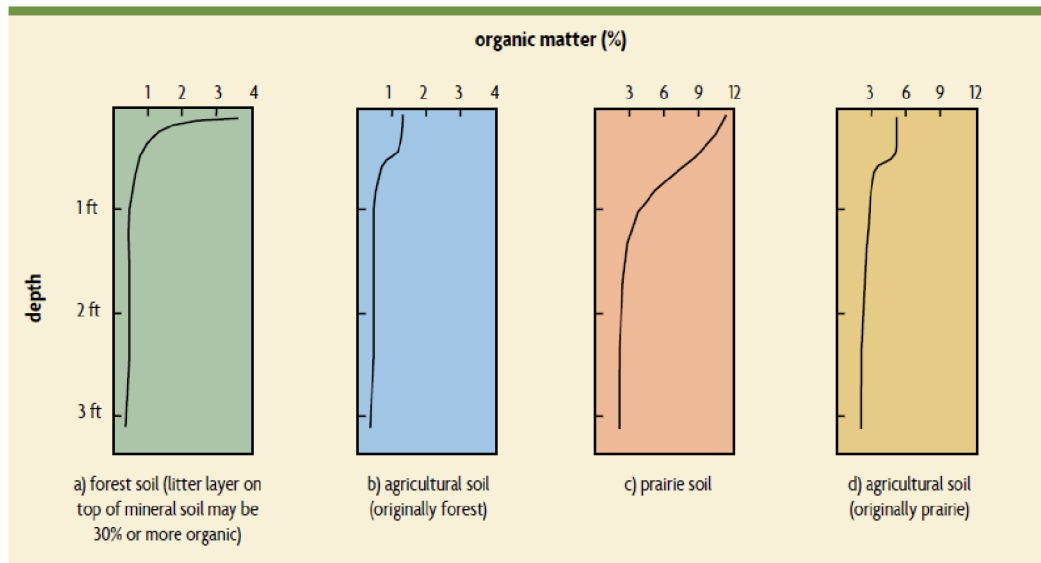
Figure 3. The distribution of SOM content in various land uses through soil profile (Magdoff & Es, 2009).

Forest tree species have significantly influenced in preserving and stabilizing organic matter in the soil (Vesterdal et al., 2013). The stabilization of the SOM has been interacted by the abiotic and biotic process (Campbell & Paustian, 2015) and takes place through these mechanisms: conservation due to recalcitrance, the interchange of metals and minerals, and unapproachable to the decomposer community due to the occlusion in the aggregate soil (Poirier et al., 2018). Additionally, it has significant influences on the changes in chemical compositions (functional groups and molecules) (Matamala et al., 2017) and decomposition of SOM due to the inputs of litter falls, root exudation, and turnover (Hobbie et al., 2007). Some studies have revealed a shift in the whole tree C allocation pattern toward the belowground soil profile with the increased atmospheric CO_2 concentration. It was also concise that a large amount of C being allocated belowground might enhance the activity of roots associated with microorganisms, more root growth and turnover, and larger microbial biomass stock and promote more microbial activities (Lal 2005; Vesterdal et al., 2013). The variation in the chemical

composition of SOM and soil nutrients within the soil profile is contingent on the forest species and biomes (Angst et al., 2016). Prescott and Grayston (2013) further emphasize that the forest tree species significantly affect the soil beneath the forest floor through many mechanisms including the leaching of nutrients and dissolved organic materials from the forest floor, permeation by roots that can alter soil physical structure and water flow, exudation of ions and organic compounds and the input of organic matter in the form of root litter.

1.2.6. Distribution of soil organic carbon stock in various regions

Globally, the forest and forest soil ecosystem consists of about 60% of the carbon contained in the earth's land surface and integral part of the global carbon cycle (Mayer et al., 2020). In table 1, it shows the difference in carbon storage in plants and soils in various biomes and land uses. The development of soil and genesis under the forest ecosystem is involved by various factors such as parent materials, types and nature of vegetation, human activities, topography, organisms, time, and climate (Lal 2015a, 2018b). These factors combined together with the development of the soil with different chemical, biological, and physical characteristics. Soil types vary worldwide but can be generally classified according to the major of forest biomes (e.g. temperate deciduous or mixed forests, boreal and coniferous forests, tropical rain forests, tropical monsoon scrub and woodlands) that are present today (Rees 2006).

Carbon storage in the forest ecosystem, on the other hand, is relatively connected with various components including biomass C and soil C (Lal 2005). Carbon sequestration and release vary across specific biomes, such as tropical, temperate, and boreal forests (Andivia et al., 2016). Tropical forests are generally characterized by the location between the 23° south and north of the equator. Tropical forests are open woodlands and dry but receive heavy rain. Temperate forests, typically located in the mid-latitudes about 50° north and south of the equator, exhibit diversity in hardwood types (oakhinory and maple-beech-birch), softwood types (Douglas-fir and lodge-pole pine), and mixed forest types (Oak-pine) (Gorte 2009). These forests contribute to a wide range of diversity of parent materials but are mildly acidic. The presence of well-decomposed organic matter can enrich the soil nutrients and accumulation of clay in the subsurface (Rees 2006). However, due to the slower decomposition rate and lower biomass production, temperate forests generally store less carbon than tropical forests, with about one-third in the vegetation and two-thirds in the soil (Vesterdal et al., 2013). Boreal forests, which are situated to the north of the temperate forests in Canada, Alaska, Scandinavia, and Russia, primarily consist of conifers like spruce, fir, and larch. Boreal forests have a low rate of evapotranspiration and a slow decomposition, resulting in thick forest floors, acidic and form on

sandy deposits from glaciation (Rees 2006). Boreal forests typically contain more carbon than tropical and temperate forests and have much higher C than other biomes except the wetland because of the short summers and high acidity of conifer forest soils (Gorte 2009). Many studies have shown that forest species, such as coniferous and deciduous forests, have various influences on soil properties, and accumulation of the SOM, and SOC in the soil profile (Cha et al., 2019; Ohno et al., 2017; Pavlů et al., 2018). Deciduous forest, with a short-term litterfall, easily accumulates the available nutrients and has highly soluble organic compounds that can improve soil microorganisms rather than accumulation of SOM (Malý et al., 2014). In contrast, the coniferous forest, with long-term vegetation, contains high-recalcitrant litter, resulting in more carbon storage and stabilizing SOM (Siles et al., 2017; Yoshida et al., 2018; Poirier et al., 2018).

Table 1. The average carbon stock under different biomes (Unit: tons per acre) (Gorte 2009).

Biome	Plants	Soil	Total
Tropical forests	54	55	109
Temperate forests	25	43	68
Boreal forests	29	153	182
Tundra	3	57	60
Cropland	1	36	37
Tropical Savannas	13	52	65
Temp. Grasslands	3	105	108
Desert/Semi-desert	1	19	20
Wetlands	19	287	306
Weighted Average	14	59	73

1.3. The other causes affecting the carbon in various biomes

The forest C stock and its distribution are influenced by both natural and human-related factors. Natural disturbances, such as wind, fire, drought, and diseases, can alter temperature and moisture regimes, and succession of forest species with various quantity and quality of biomass that return to the soil (Kavdir et al., 2005). Events like fire can change the canopy cover resulting in SOC loss on the surface layer through rainfall and erosion, and has a long-term effect on C stock in the forest (Six et al., 2004). The impacts of fire on SOC stock depends on the fire temperature and duration, SOC stock and its distribution in the soil horizon and the changes in the decomposition of SOM (Silva et al., 2022). For instance, forest fire in tundra regions can shift a net C sink into a net C source. During

the forest fire, about 50% or more of organic carbon on the surface is consumed and the forest fire rearranges the C into a new form and distributed it into the deeper soil profile (Mayer et al., 2020).

Anthropogenic disturbances, including atmospheric acid deposition, forest management, deforestation, afforestation, and subsequent management of the forest plantations, also affect SOC content in the forest soils (Bentsi-Enchill et al., 2022; Berhe et al., 2018; Berthrong et al., 2009; Llorente et al., 2010). Afforestation and reforestation, along with proper management, can enhance soil carbon stock. Reforestation in the abandoned agricultural regions can increase SOC stock significantly by roughly around 117 Mg ha^{-1} under 27-year-old pin oak forest and 227 Mg ha^{-1} under 69-year-old beech forest. However, the average of SOC stock in the mineral horizons increases after afforestation by roughly 0.8 Mg C (ha/year). The afforestation in reclaimed mine soil, however, has a strong impact on the SOC, as highlighted by Lal (2005). Atmospheric acid deposition, on the other hand, alter the soil organic carbon accumulation (Oulehle et al., 2007) and adversely affects soil chemistry and forest ecosystem by increasing the proton H$^+$, causing strong soil acidity that can deplete the base cations and promote the mobilization of Al and other potential toxic elements into the soil (Figure 4) (Likens et al., 1996; Liu et al., 2022; Johnson et al., 2018). Conversely, several studies indicated acid rain could increase the accumulation of C and soil C sequestration by suppressing the decomposition foliar litter and SOC, decreasing soil microbial biomass carbon, and increasing dissolved organic carbon in the uppermost layers; therefore, reducing soil respiration (Radoslava et al., 2014; Wu et al., 2016; Liu et al., 2022).
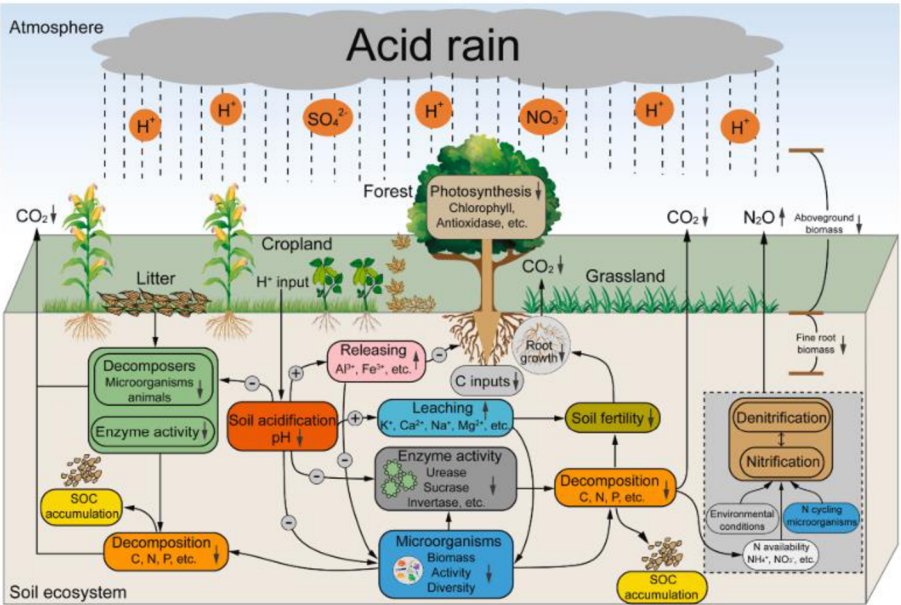

Figure 4. The mechanism underlying the effects of acid rain on soil C in the forest soil (Liu et al., 2022).

1.4. Elements cycle in the forest ecosystem

In the natural forest, the element cycle is an essential aspect as an amount of nutrients return to the soil through processes like litterfall, root exudation, and decomposition of organic matter by microorganisms (Sharma & Sharma, 2004). The process of terrestrial element cycling can be estimated upon the ratio of the element in the environment and element partitioning and turnover of the aspects in the microbial biomass (Spohn 2016). However, the processes of the element cycles in the forest ecosystem occur in two different ways, namely (1) an internal biological cycle and (2) an external geochemical cycle. **In the biogeochemical cycle,** it refers to the transport of bio-elements between soil and plant and the repeated use in plant metabolism and animals (Rivera-monroy et al., 2017). There are two main pathways. First, from trees to the soils, the nutrients are transported to the forest floor via leaf/litter fall, twigs, fruit, and flower drops. For instance, if the ecosystem production exceeds decomposition, then the nutrient storage would occur as biomass accumulation. But, if the decomposition predominated, then the nutrients are released through the decomposition of organic residues (Likens et al., 1981). The second pathway is the movement of the nutrients from the soil to the tree through the activities of the root system. The main components of the nutrient cycles are transfer, release, and retention in the forest stands. In table 2, it shows the examples of typical tree species that uptake, retain and return the nutrients in the ecosystem. **In external geochemical cycle**, it focuses on the input of the nutrients that transport in various ways such as precipitation, weathering of rocks, biological N_2 fixation, fertilization and other output of nutrients through harvest, volatilization, leaching, forest fire, erosion, and drainage (Sharma & Sharma, 2004). The scale of the movement is large, often continental, or even global because the storage and the transport can be significantly different across the ecosystem. On the other hand, a comparison of element input from the atmosphere and element outputs leaching from the bottom of the root zone can also estimate the fate of accumulation and release of nutrients such as Ca, Mg, K, S, N, and Al in the forest ecosystem (de Vries et al., 2007). Figure 5 shows the conceptual overview of the translocations and biochemical processes in the forest ecosystem.
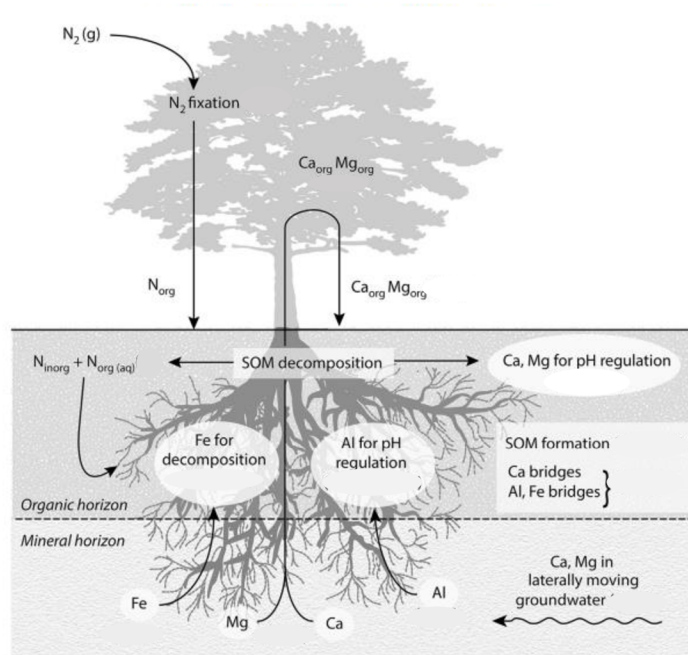
Figure 5. The conceptual overview of the translocations and biochemical processes in the forest ecosystem (Clarholm & Skyllberg, 2013).

Table 2. Nutrient uptake, retained and returned under different tree species (Sharma & Sharma, 2004).

Species		Nutrients (kg/ha)		
		N	P	K
Pinus Sylvestris (mature)	Uptake	50	4	4
	Retained	10	1	2
	Returned	35	3	4
Fagus Sylvatica (mature)	Uptake	50	12	14
	Retained	10	2	4
	Returned	40	10	10
Pseudotsuga Menziesii (37 yrs)	Uptake	39	7	29
	Retained	24	6	14
	Returned	14	1	15
Pinus patula (12 yrs)	Uptake	51	3	22
	Retained	29	3	15
	Returned	22	<1	7
Eucalyptus. globulus (10 yrs)	Uptake	101	7	76
	Retained	43	3	36
	Returned	58	4	40

1.5. Humic substances

Humic substances (HS) can be described as the organic material mainly widespread in nature (Trevisan et al., 2010). Their behavior in terrestrial ecosystems varies based on factors such as parent

materials, vegetation types, climate conditions, land use, and topography (Ussiri et al., 2003; Senesi et al., 2003). HS, however, significantly affects the chemical sorption, the capacity of soil buffering, micronutrient availability, and alleviation of trace elements and metal deficiency in the soil (Guimarães et al., 2013; Tang et al., 2014; Tunega et al., 2020). The humus formation can be identified as a morphological pattern observed in the association of the organic matter with the mineral matter at the uppermost horizon (Ponge 2003; Delft et al., 2006). The humus formation occurs with various polymerization pathways of the precursors like polyphenols, quinone compounds, saccharides, and nitrogenous compounds (Wu et al., 2020). Besides that, a key characteristic of HS is based on their ability to interact with metal ions, oxides, hydroxides, minerals, and organic compounds, including toxic pollutants to form water-insoluble and water-soluble complexes (Trevisan et al., 2010; Pospíšilová & Fasurova, 2009). In Figure 6, it shows the processes of HS formation through the soil profile and also classification of the humus types (Mor, Moder, and Mull). Many researchers reported that the humic substances in dissolved forms or mineral-bound surfaces enhance the sorption of organic compounds in the soil (Al-Farsi et al., 2017; Trevisan et al., 2010).
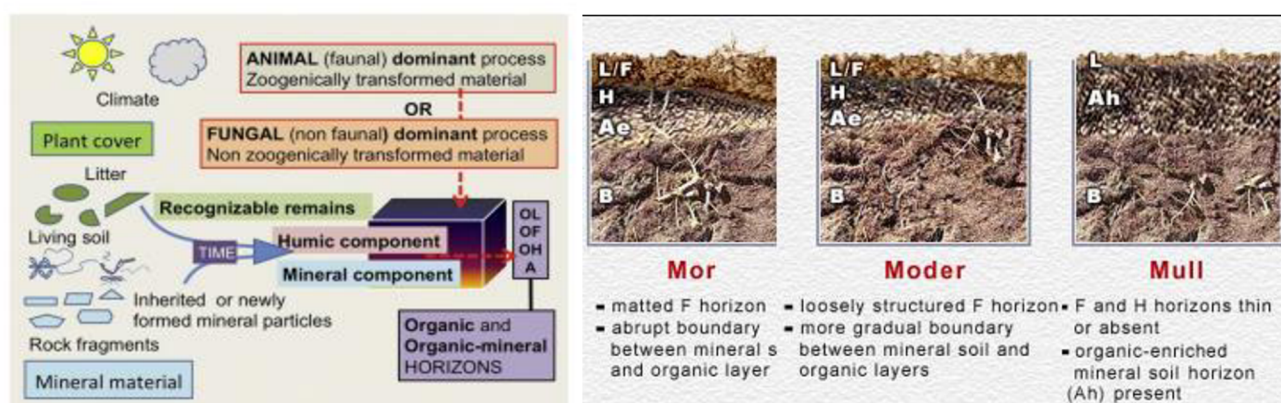
Figure 6. The formation of humic substances and examples of humus forms under different horizons (MoF 1997; Zanella et al., 2018).

In the last two decades, the view of the structure of HS has been developed and varies in recent research (Pavlů et al 2023), which you can find the different humic substance structures in Figure 7. In the early concept, HS consisted of a system of polymers depending on the observation that exchange acidities, elemental composition, optical properties, molecular weight characteristics, and electrophoretic properties and differed consistently with the soil types (Piccolo 2002). The polymers concept of HS includes the idea of polydisperse by which HS is composed of polymers containing various molecule weights, which is relatively similar to other natural biological macromolecules (e.g., lignin, proteins, carbohydrates) (Piccolo 2002; Yang et al., 2004; Debska et al., 2007). On the

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contrary, Piccolo (2002) reviewed that HS could be better described as a supramolecular association than being constituted by macromolecular polymers, as the traditional concept believed. A new view of the humic substances has been described as the supramolecular associations of relatively small humic and chemically diverse organic molecules linked together by hydrogen bonds and hydrophobic interaction (Sutton & Sposito, 2005; Gerke 2018). A model of humus as a supramolecular association, which is derived from the extended microbial decomposition of various dead materials and animal biomolecules, combines mainly hydrophobic forces strengthened by the hydrophobic effect. These forces can also stabilize the structure of molecular aggregates. The HS aggregate stability tends to be dynamic and influenced by the solution of ironic strength and pH. At the high pH (alkaline), the HS is in dispersed form because intramolecular hydrogen bonding is disrupted. At the lowest pH, which is smaller than 3, the HS collapses into smaller aggregates. This occurrence is because of the protonation of carboxylate groups that favor an increase in number of intra- and intermolecular hydrogen bound inside the humic macromolecules (Trevisan et al., 2010).

Macromolecules concept   Supramolecular association concept
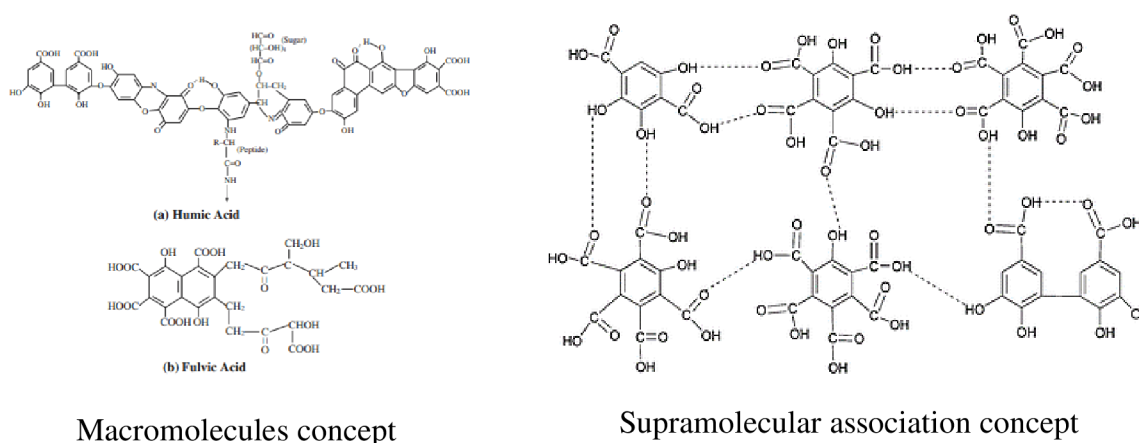
Figure 7. The humic substances structure by macromolecules and supramolecular associations concepts (Wang & Mulligan, 2006; Piccolo 2002).

On the other hand, Lehmann and Kleber (2015) reviewed and argued that the terminology of HS in soil science led to misinterpretations or varying definitions from researchers. Therefore, the HS in our study was interpreted according to Piccolo's review. For a similar reason, we used the description of 'alkaline extractable organic substances (AEOS) for a mixture or an association of compounds extractable with alkaline solutions. It is especially important in surface horizons, where these compounds could not be present in the classical concept of humification processes. Extracts from L and F horizons contain a mixture of organic compounds such as lignin, carbohydrate, protein, lipid, and carbonyl due to the fresh and non-decayed materials.

The AEOS can be subdivided into low soluble (soluble only in alkaline nature and in mineral horizons, also called humic acids (HA)), soluble (soluble in whole pH scale and in mineral horizons, also called fulvic acids (FA)) and unextractable (humin). HA and FA have been ascribed as the main components of humic substances and have similar structures and compositions (Ribeiro et al., 2001). HA and FA are relatively important complexing ligands for most metal ions in the terrestrial ecosystem (Porcal et al., 2009; Zhou et al., 2014). The quality and quantity of the HA and FA depend on their origins and the degree of SOM maturity (Debska et al., 2007; Machado et al., 2020; Banach-Szott et al., 2021). HA and FA, generally, differ in molecular weight, functional group, and element content. HAs are typically higher in molecular weights and contains less oxygen-containing functional groups than FA (Tang et al., 2014).

HA are soluble in a pH greater than 2 and can be called as polycondensed polyphenol compounds with functional groups, heterocyclic rings, and methylene bridges, which could influence the decomposition and bioavailability, and bioaccumulation (Ribeiro et al., 2001). The FA is composed of low molecular weight compounds with simple structures, which are soluble in water in any pH conditions (Allard 2006). FA is considered the most variable and mobile fraction of humus substances in the soil (Bai et al., 2015). The HA and FA behave differently through the soil profile due to the decomposition rate, mobility, and chemical sorption. Porcal et al. (2009) reviewed that the HA:FA ratio decrease through the soil profile in podzolic soil could reflect the reduction of mobility and degradation of HA. Conversely, once it occurs in cambic soil, the degradation of and mobility of HA are twice higher values in A- and AB-horizon than in B-horizon. Ussiri et al. (2003) found that HA was less acidic compared to FA and had higher aliphatic and phenolic compounds content than FA.

1.6. Methods for characterizing SOM structures

1.6.1. Infrared spectroscopy

Infrared spectroscopic techniques are non-destructive and rapid techniques used to identify the different biochemical components in organic material (Chapman et al., 2001). In practice, there are two main spectral regions used, namely the near-infrared region (NIR) and the mid-infrared region (MIR). It is commonly used to analyze peat soil, composts, and the transformation of organic matter during composting within various stages (Zaccheo et al., 2002). However, MIR diffuse reflectance spectra are recognized for distinguishing the fluctuation in the abundance of organic functional groups during the decomposition and identifying the changes of SOM in the soil profile under different vegetation covers (Veum et al., 2014; Tinti et al., 2015). Fourier transform infrared (FTIR)

spectroscopy is spectroscopic techniques and is the form of vibrational spectroscopy that is useful in the study of a variety of soil chemical processes (Margenot et al., 2016). FTIR can provide fundamental information on the molecular structure of organic and inorganic components (Berna 2017). In FTIR analysis, the absorption of IR radiation occurs when a photon transfers to molecule and excites it to a higher energy state, resulting in the vibration of molecule bonds such as bending, twisting, stretching, rocking, and wagging that occurring at varying wavenumbers (Figure 8) (Chen et al., 2015). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra is also a spectroscopic technique what can be used for various soil/site properties including parent materials, land cover types, bulk density (BD), cation exchange capacity (CEC), pH, soil depth, and the concentration of C and N (Matamala et al., 2017). DRIFT spectra, in addition, were strongly connected to the decomposition of SOM, particularly to the organic horizons regarding the ratio of the band and/or absorption of the specific spectral band of soil. For example, the absorption band at 2922 cm^{-1} can be used to investigate the total organic carbon (TOC), total carbon (TC) and total nitrogen and the ratio of C:N quickly (Matamala et al., 2017).
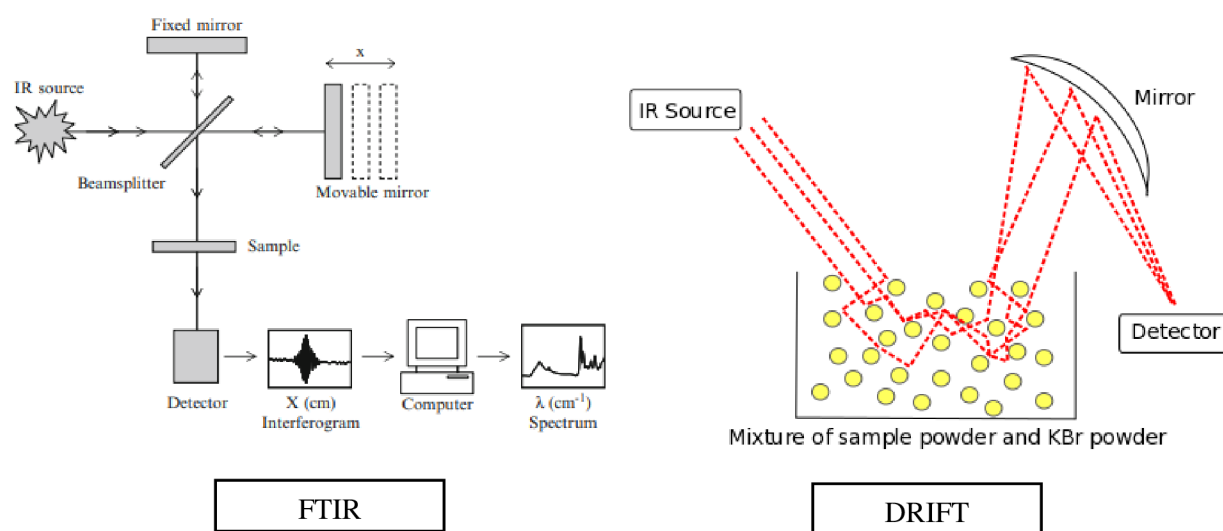
Figure 8. The schematic of FTIR and DRIFT spectroscopy (Chen et al., 2015; Ojeda & Dittrich, 2012).

DRIFT methods involve the interaction between molecular subcomponents and electromagnetic radiation in the functional groups. Spectroscopic light transfers its energy to the molecular subcomponents during the interaction of wave particles (Ellerbrock & Gerke, 2013). Generally, wave-particle dualism plays an essential role in all spectroscopic methods due to the provision of a push and a probability of transferring energy by the dualism light of wavelength to subcomponents (atom, protons, and electron). The molecule of subcomponent can be moved to a greater level of energy. The

energy level of subcomponents is influenced by the types of functional groups, which can be ascribed (Ellerbrock & Gerke, 2013).

DRIFT spectroscopy has been used in many fields such as the chemistry of waste and compost materials, characteristics of chemical compounds in clay, forest litter decomposition, soluble SOM fraction, hydrophobicity of organic matter (Capriel 1997), and the influence of site and soil properties on organic matter transformation in the peat soil column (Matamala et al., 2017).

Soils are quite complex and contain many different components and properties such as silicate, sulphates, nitrates, carbonates, phosphates, humic and fulvic acids, cellulose, fats, lipid, lignin, carbohydrates, protein, etc. (Śliwińska et al., 2019). The FTIR spectra illustrate the absorption bands characteristic depending on the types of molecular bonding in OM functional groups or other chemical properties (Ellerbrock & Gerke, 2013). So the bands from the spectra change and fluctuate according to the content of quartz, clay, organic compounds, and humic substances in the soil (Śliwińska et al., 2019). The following text illustrates the identification of properties of different soil types (soil minerals, humic substances, and SOM) through FTIR spectroscopy.

1.6.2. Identification of soil components by FTIR

FTIR spectroscopy effectively distinguishes mineral soil characteristics, including quartz, alumosilicates, silicates, and clays (Matamala et al., 2017). The intensities and positions of the band in soils are presented in Table 3 and they could be associated with OH stretching (H bonded water), exchangeable cation, bending vibration, Si-O groups stretching, and quartz overtone. For instance, the strong band at 3616 cm^{-1} on the clay mineral soil results from the OH stretching vibration of the OH structure group and broadband at 3423 cm^{-1} results from the asymmetric overlap and symmetric (O-H-O) vibration of H bounded water (Madejová 2003).

FTIR is quite suitable for describing the features of SOM through the specific peak of soil spectra that are listed in Table 4. Additionally, the characteristic of SOM spectra has been identified by intense or overlapping bands. Similar position bands are used for evaluating humic substance structure (freeze-dried powder samples), where the positions of the bands are mentioned in Table 5 and Figure 9.

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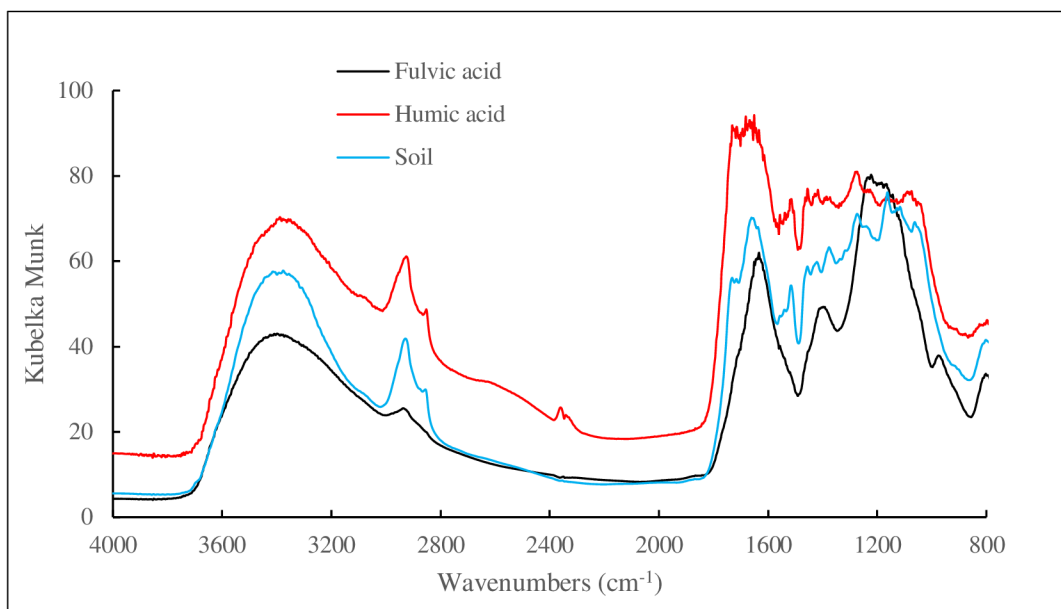
Figure 9. The example spectra of humic and fulvic acid and soil sample from F horizon of forest soil.

Table 3. The peaks and spectral bands investigated by FTIR spectra of the mineral soil components (Tinti et al., 2015; Yeasmin et al., 2020).

Peaks cm^{-1}	Band range cm^{-1}	Assignment
3698	3719-3685	Si-O-H vibration of clays, kaolinite, and Fe oxides
3622	3682-3577	Si-O-H vibration in clays, kaolinite, gibbsite, and Fe oxide
~3640	3525-3460	O-H stretching of gibbsite
~3430		O-H stretching of H-bonded water
2627		Aragonite (overtone/combination band)
2592		Calcite (overtone/combination band)
~2520	2562-2480	Carbonate ($CaCO_3$) (overtone/combination band)
~2000	2000-1790	Si-O vibration of quartz mineral (overtone/combination
1800		band)
	1642-1569	Calcite (overtone/combination band)
	1479-1408	OH bending of water
	1293-1256	Carbonates
1238		Bentonite
	1136-1070	Silicate
	1056-945	O-Si-O stretching of silica, sulfates
920		Si-OH of alumino-silicate lattice (kaolinite, illite, smectite)
	887-866	Al-OH deformation of kaolinite
	820-752	Carbonate

720		Inorganic materials (clay and quartz minerals) carbonate,
700		kaolinite
650		Calcite
520		Silica
470		Bentonite
		Si-O-Al bending

Table 4. The peaks and bands of spectra in the SOM investigated by FTIR spectroscopy (Capriel 1997; Tinti et al., 2015).

Peaks cm^{-1}	Band range cm^{-1}	Assignment
	3440-3320	O-H and N-H stretching, H-bonded OH
	3107-3042	Aryl, $R_2C=CH_2$, $R_2C=CHR$
2930	3010-2800	Aliphatic CH stretching
1730-1700	1775-1711	C=O stretching
~1650	1691-1642	C=O stretching of amides (amide I), H-bonded conjugated ketones, carboxyls and quinones, lignin, C=N stretching
	1642-1569	Amide II of primary amides, aromatic C=O, C=O (quinones), carboxylates and amides, $R-O-NO_2$
1530-1510	1544-1488	Aromatic C=C stretching, aromatic skeletal vibration, aromatic (lignin), amide II
	1479-1444	CH and NH of amide II, aliphatic CH deformation
~1415	1444-1408	Benzoic acid, C-H deformation, and C-O stretching of phenolic groups
1380	1403-1354	C-O of phenolic OH, COO$^-$ and O-H, CH_3 bend, $COCH_3$
	1342-1307	Sulfonamides, C-N (aromatic amines)
	1293-1256	Benzoic acids, C-O of aryl ethers, R-O-NO2, P=O, C-O of phenols, C-O-C ether bond, amide III
~1230	1256-1198	C-O stretching and OH deformation of COOH, C-O of aryl ethers and phenols, acetates
1160	1185-1144	C-OH of aliphatic alcohols, carbohydrates
	1136-1070	C-O of various alcohol types, C-O of alkyl ethers C-OH
	1056-945	

	945-887	C-O stretching (1080-1030, carbohydrate region of polysaccharides, RHC=CH$_2$) sulfones, P-O aryl, P-O
870		alkyl, aromatic CH out of plane bending
835		Benzoic acid, pyranose ring (carbohydrates), cellulose
	820-752	(ring breathing), RHC=CH$_2$, R$_2$C=CH$_2$
		aromatic C-H and C=C
		R$_2$C-CHR, phenyls with three H adjacent

Spectral peaks serve as a basis for diverse methods to estimate SOM composition (Tinti et al., 2015). They play a crucial role in determining the hydrophobicity of organic matter in a huge number of arable land with different content of organic carbon and soil textures (Capriel 1997). Methyl, methylene, and methine groups, existing in aliphatic C-H groups, have a strong influence on hydrophobicity. It can be defined as hydrophobicity index (HI) to describe the degree of hydrophobicity of SOM. The symmetric and asymmetric stretching vibration of the aliphatic groups generally absorb in the range of infrared spectra from 3000 to 2800 cm^{-1} (Capriel et al., 1995). The aliphatic C-H groups manage the water affinity by stabilization of microbial, adsorption, and wetting. These effects extend their influence over microbial biomass, organic matter, dissolved organic matter, aggregate stability, leaching, water infiltration, and chemical properties. Aside from that, FTIR spectra can be used to determine the hydrophilic groups C-O in organic matter (Ellerbrock & Gerke, 2013) and prevent C=C and amide bands from overlapping (Onweremadu & Anikwe, 2007). Ellerbrock et al. (2005) stated that FTIR spectra were analyzed at absorption bands that indicate relatively hydrophobic (3000-2800 cm^{-1}) and hydrophilic (1740-1698 and 1640-1600 cm^{-1}) OM functional groups.

Table 5. The assignment of the adsorption bands of humic and fulvic acids in infrared spectra (Stevenson 1994; Tatzber et al., 2007; Pavlů & Mühlhanselová, 2017).

Band range (cm^{-1})	Assignment of sorption bands
3400–3300	O–H stretching, N–H stretching
2950–2800	Aliphatic C–H stretching
1725–1710	C=O stretching of COOH and ketones
1660–1630	C=O stretching of amide I, quinone, H-bonded conjugated
1620–1600	Aromatic C=C stretching and H-bonded C=O
1590–1517	N-H bending and C=N stretching (amide II)
1470–1380	Aliphatic C–H bending

1400–1390	OH deformation and C-H stretching of phenolic OH, C-H deformation of CH_2 and CH_3 group
1280–1200	C–O stretching and OH deformation of COOH,
1170–950	C–O stretch of carbohydrate, polysaccharides, alcohol, and ester

2. Scientific hypothesis and objectives

2.1. Hypotheses

a) SOM stabilization in the soil is closely associated with land use.

b) Chemical and mechanical SOM stabilization exist in parallel in soil profile, but their portions are different in different soil horizons and soil types.

c) SOM stabilization in the soil is connected with the chemical composition of incoming fresh organic matter and responds to changes in vegetation cover over time.

2.2. Objectives

The research aimed to specify SOM qualitative parameters in all the soil depths. SOM content in different soils such as crop soil, grass soil, and forest soil were used to compare with specific surface organic horizons. Temporal and spatial changes in SOM composition and different ways of SOM stabilization have been studied. The main goals are:

1) To evaluate the SOM composition changes in the entire soil profile.
   Fulfilled in the published paper in sections 7.1, 7.3, 7.4 and 7.5

2) To evaluate interrelationships of the organic and mineral phases of the soil
   Fulfilled in the published paper in sections 7.2, 7.4

3) To evaluate the forest litter composition changes during the time.
   Fulfilled in the published paper in sections 7.3 and 7.5

4) To compare the SOM originated from different incoming fresh materials.
   Fulfilled in the published paper in sections 7.1, 7.2, 7.3, 7.4 and 7.5

3. Materials and methods

3.1. Site selection

In Suchdol, the study focused on three different land uses such as cropland, grassland, and forestland. The area is situated 380 m a.s.l. and has a mean annual precipitation of about 470 mm and the mean average temperature of 8 °C. The mixture of loess and sandy river sediments of the Quaternary age creates the bedrock of the study area. Haplic Luvisols are the prevailing soil type in all land uses. Cropland site (with a dominantly grown wheat (*Triticum aestivum* L.) crop interspersed with rape (*Brassica napus* L.) and maize (*Zea mays* L.)) marginally include the areas of greyic Phaeozems and carbonates were detected in several soil samples mainly in deeper layers. Soil texture belongs to the clay loam category. The same soil description applies to grassland site (poorly maintained grassland with *Dactylis polygama Horv., Poa annua* L., *Calamagrostis epigejos* Roth). Broadleaf forest site with the dominant abundance of oak (*Quercus petraea (Matt.) Liebl.*) followed by beech (*Fagus sylvatica* L.), and hornbeam (*Carpinus betulus* L.) marginally include the areas of Regosols and Cambisols. The presence of carbonate was not detected in all soil samples from the forest. Soil texture belongs to the sandy clay loam category. These sites were selected based on different compositions of incoming fresh organic material, which could manifest itself in the composition of organic matter in the whole soil profile.
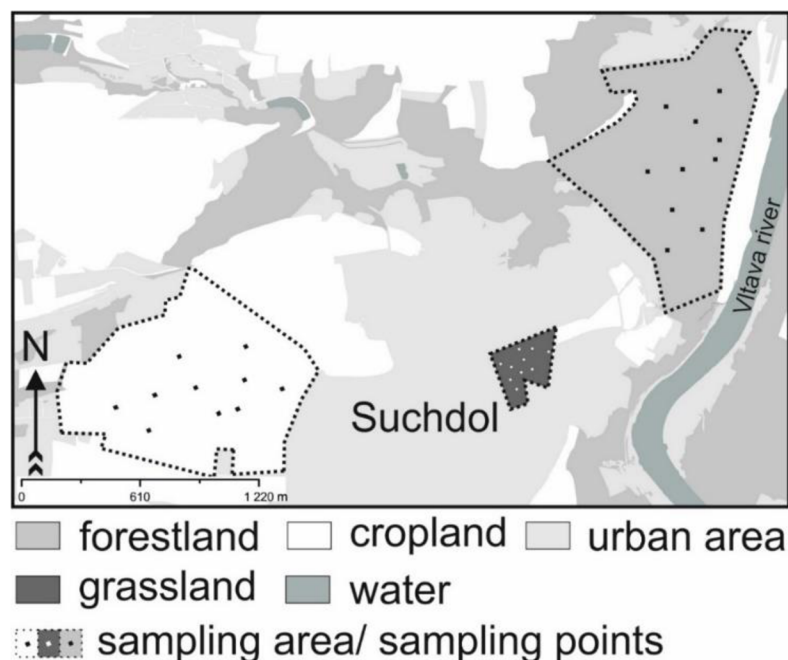

Figure 10. Localization of research sites on cropland, grassland, and forestland in Prague Suchdol.

In the Jizera Mountains, the research focused on two different forest species (beech and spruce). It is located in the northern part of the Czech Republic along the border with Poland. The region was heavily affected by acid deposition mainly during the 1980-1990 period because of the nearby coal-fired power plant (black triangle – Czech-German-Polish border) (Moldan and Schnoor, 1992). Sampling site is called Paličník (50.8683900N, 15.2527000E), where it has been monitored for a long time (Borůvka et al., 2009; Tejnecký et al., 2010, 2013); therefore, it was selected also for this research. The elevation of the sampling locality ranges from 635 to 680 m a.s.l. The average annual precipitation is around 1200 mm and the average temperature is roughly 4-7 $^{\circ}$C (Remrova & Císlerová, 2010; Balcar et al., 2012). The vegetation is dominated by the European beech (*Fagus sylvatica*) within the natural ecosystem of the occurrence of perennial grasses in ground vegetation (*Calamagrostis arundinacea*, *Calamagrostis villosa*) and spruce monoculture forest (Norway spruce: (*Picea abies* (L.) Karst.) along with perennial grasses (*Calamagrostis arundinacea, Calamagrostis villosa*). The average height of the forest stands is about 32.4 m in beech forest and 28.6 m in the spruce forest (Bradová et al., 2015). Additionally, the soils were characterized as dystric Cambisol under beech forest and entic or Haplic Podzol under spruce (Tejnecký et al., 2010, 2013, 2014). Soil bedrock was determined as medium-grained porphyritic biotite granite to granodiorite according to the geological map (Cháb et al., 2007).
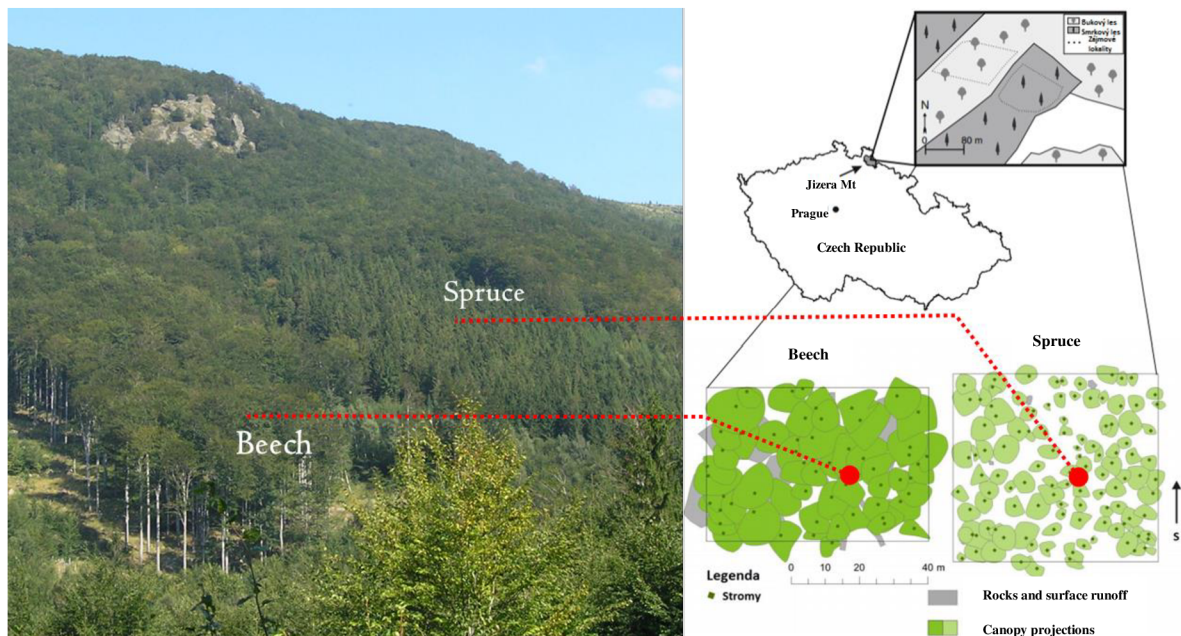

Figure 11. Localization of research sites on forest cover, beech and spruce – Jizera Mountains.

In Troja, the research focused on the effect of using different organic mulched on soil aggregates. The study site was carried out at the university experimental field in Troja, Prague, Czech Republic. The locality is situated along the Vltava River at an altitude of 196 m. The average annual precipitation is 470 mm, and the annual average temperature is 11 °C. The soil is characterized as Haplic Fluvisol (IUSS Working Group WRB 2014) with sandy loam texture. The experimental design and soil sampling descriptions were described in detail by Pavlů et al. (2021). Twenty-seven plots (each with an area of 4.5 m^2) were prepared. Mulches were applied to 24 plots, eight mulch types (bark chips, wood chips, wheat straw, cardboard, paper foil, decomposable matting, nonwoven fabric covered by bark chips, and crushed basalt) in three replications and 3 plots remained as control without mulch. The plots were planted with six perennials, always in the same area scheme (*Geranium sanguineum, Hemerocallis, Salvia nemorosa, Echinacea purpurea, Coreopsis verticilata, and Heuchera sanguinea*) and without adding any fertilizers.

Colluvisols were observed in three localities (Brumovice, Vidim, and Kosova Hora) fundamentally different in their geological and pedological conditions, climate, and settlement history but with similar topography. Brumovice is situated in a loess region in South Moravia in the Czech Republic. The average annual temperature varies between 9 and 10 °C, and the average annual precipitation is between 500 and 550 mm. The history of this site and Colluvisols forming conditions are described by Zádorová et al., (2013, 2023) and detailed soil description by Chlupáč et al., (2002) and Jakšík et al., (2015). Areas with minimal slope (0–2°) are covered mainly by Calcic Chernozems, areas with increasing slope by its eroded forms, and the steepest parts (8–15°) of the slopes by Regosols and Calcisols. Loess itself is exposed in many cases. Colluvial soils (Kastanozems and Phaeozems (Solimovic) with deep humus horizons are formed in slope depressions (Zádorová et al., 2013). The research was performed on an agricultural parcel (area of 6 ha), forming a complex slope system with different landforms. Vidim is situated in Central Bohemia (Czech Republic), in the Pšovka River watershed. The wider area is underlain by Cretaceous sandstones covered by a Pleistocene loess layer (Chlupáč et al., 2002). Haplic and Albic Luvisols are the original dominant soil units. The average annual temperature varies between 7 and 8 °C, and the average annual precipitation is between 550 and 650 mm. The study plot (4.5 ha of agricultural soil) is characterized by intensive topography dominated by two side valleys connected in the southwest part of the site. These two concave units represent the main accumulation positions at the plot, where colluvial soils (Haplic Luvisols (Solimovic) developed. The adjacent slopes, covered by eroded Luvisols and Regosols, are relatively. Kosova Hora is situated in the central part of the Czech Republic in the Central Bohemian Upland. Geologically, the area forms part of Central Bohemian magmatic pluton. The parent material of the

study area derives from granodiorites, in the side valleys covered by silty deluvial sediments (Chlupáč et al., 2002). The average annual temperature varies between 7 and 8 °C and annual precipitation is between 600 and 700 mm. The study plot covers an area of 10 ha of agricultural soil. The terrain is complex comprising of backslopes, a side valley, and two significant colluvial–alluvial cones at the toe-slopes. Eutric Cambisols are the dominant soil units, significantly eroded at the slopes. Zádorová et al. (2023) described the occurrence of Luvisols in the study area, namely in the flat parts of the terrain. Skeletic Leptosols occur at the steepest parts. Stratified Colluvisols (Solimovic Cambisols) developed in concave positions.

3.2. Soil sampling and soil preparation

In Suchdol, the soil samples were taken during April and May 2018. Ninety disturbed soil samples were collected at three different depths (0-10, 10-20, and 20-30 cm) using auger. All samples were collected in S shape to estimate the average organic carbon content in the whole area. The grass and residues were meticulously removed before sampling. In Jizera Mountains, the soil samples were taken in four different years (June 2008, n = 24; June 2013, n = 24; Sept 2015, n = 56; and Sept 2020, n = 24). At each species site (Beech and Spruce), three individual soil pits (50 x 50 cm) were dug in 2008, 2013, and 2020, while seven soil pits were dug in 2015. The soil samples were taken in different soil horizons: litter horizon (L), fragmented horizons (F), humified horizons (H), organo-mineral humic horizons (A), and subsurface mineral horizon (B) (cambic horizon under beech, spodic humusosesquioxidic horizon and cambic horizon enriched with iron oxides under spruce). The particular soil pits were randomly selected and the distance between soil pits was at least 15 m. In Troja, grab soil samples from 4 punctures per each plot were collected from the surface layer (0–10 cm) using a gouge auger. Samples for aggregate extraction were carefully collected separately using a plastic shovel. Soil sampling was carried out after perennials cutting in October 2018 (last year of experiment). Only the samples from plots mulched with straw, bark, and wood chips were selected and used for this study, because of the significant effect of these mulches on water stable aggregates (WSA) index (Pavlů et al. 2021). Samples from the same year and from control plots were selected and used for a comparison. In Brumovice, Vidim, and Kosova Hora, soil samples were collected from four soil pits in each area. One pit always captures soil negligibly affected by erosion in the higher and flatter parts of the area. The second was dug in the most eroded sloping part of the area. The remaining two were located in places of accumulation of eroded material (toe-slope and side valley). Soil samples were taken every 10 cm down to the depth of the original soil-forming substrate or in-situ soil material.

Subsequently, the collected soil samples were air-dried and sieved with a 2-mm sieve to remove the debris, rocks, and stones from the samples. The soil samples for measuring with infrared spectroscopy were finely milled with a Fritsch Analysette 3 Spartan Pulvensette miller, Idar-Oberstein, Germany. Additionally, some portions of soil samples were stored in the freezer for further analysis of specific chemical composition such as dissolved organic carbon (DOC) and low molecular mass of organic acid (LMMOA). Samples for aggregate extraction were air-dried and aggregates of diameter 2–5 mm were extracted by sieving. The size of the aggregates was chosen in accordance with WSA measuring procedure (Nimmo & Perkins 2002). These aggregates were then crushed for chemical analysis.

3.3. Soil organic matter analysis

For the chemical soil analysis, we present mainly the determination of SOM characteristics (i.e., Humus quality, DOC, LMMOA, SOC, HA, FA, spectral analysis etc.). Other details about basics soil characteristics determination were present in published articles.

3.3.1. The humus quality

The humus quality (E4/E6) was assessed through the spectrophotometric method. Two gram of 2-mm sieved soil samples were extracted using 40ml of 0.05M $Na_4P_2O_7$ in a 100 ml PE bottle, shaken for 1 hour, and then centrifuged. The absorbance ratio of supernatant was measured at 400 and 600 nm (Sparks 1996, Agilent 8453 UV Visible spectrophotometer, Santa Clara, USA). The higher E4/E6 ratio indicates a lower degree of humification processes (Kunlanit et al. 2019). E4/E6 value of 3.6 corresponds to a HA:FA ratio of 1.

3.3.2. Dissolved organic carbon and low molecule mass organic acids

Fresh samples were subjected to deionized water extraction (ratio soil/water 1:10 w/v, 1 h extraction on a reciprocal shaker at a stable laboratory temperature of 20 °C). The suspension was then centrifuged at 4000 rpm for 10 min and the extracts were filtered through 0.45 μm nylon membrane filters. Aqueous extracts were then analyzed for pH, DOC, the content of LMMOA and inorganic anions using ion chromatography (IC). Additionally, the content of selected elements was assessed using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

For DOC determination, 2 ml of the extracted samples was mixed with a mineralization chromium-sulphuric acid mixture (3 ml) and then heated at 135 $^\circ$C for 45 minutes. The absorbance of soil extracts was measured at 340 nm (HP spectrophotometer, Hewlett Packard 8453, USA). The DOC content

was determined by calculation from the calibration curve. Besides that, the soil moisture content was also measured for recalculation of the content of DOC as mg kg^{-1} dry soil.

LMMOA, including quinate, lactate, acetate, propionate, formate, isobutyrate, butyrate, isovalerate, valerate, adipate, malate, tartrate, maleate, oxalate, fumarate, citrate, isocitrate, cis-aconitate, trans-aconitate, were analyzed via capillary ion-exchange chromatography with suppressed conductivity (capillary high-pressure ion chromatography - HPIC). Dionex ICS 4000 (Thermo Scientific, USA) system equipped with Dionex IonPac AS11-HC 4 μm (Thermo Scientific, USA) guard and analytical columns was used. The eluent composition was the following: 0-10 min isocratic: 1 mM KOH; 10-20 min concave gradient: 1-10 mM KOH; 20-30 min concave gradient: 10-20 mM KOH; 30-40 min concave gradient: 20-40 mM KOH; and 40-60 min linear gradient: 40-70 mM KOH. The flow rate was set to 0.012 mL min^{-1}. To suppress eluent conductivity the ACES 300 suppressor (Thermo Scientific, USA) was used. To suppress carbon dioxide baseline shift the Carbonate Removal Device 200 (Thermo Scientific, USA) was implemented.

Chromatograms were evaluated and proceeded using the software Chromeleon 7.20 (Dionex, USA). Standards were prepared from 1 g L^{-1} anion concentrates (Analytika, CZ and Inorganic Ventures, USA) and deionized water (conductivity < 0.055 μS cm^{-1}; Adrona, Latvia) in the range of 0.1- 40 mg L^{-1}. The concentration of extracted elements was determined using ICP-OES (iCAP 7000, Thermo Scientific, USA).

3.3.3. Soil organic carbon

The SOC content was determined by rapid dichromate oxidation ($K_2Cr_2O_7$) techniques following Tyurin´s method (Sparks 1996). The 0.25-mm sieved soil samples were weighted in between 0.05–0.4g and added 10 ml of the mixture of potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4). The varied soil sample weights were based on organic carbon content in the soil. The soil solution was heated in the oven at 125 $^{\circ}$C for 45 minutes. Subsequently, the solution with dichromate was titrated potentiometrically with the Mohr salt $(NH_4)_2 Fe(SO_4)_2$ with stirring for homogeneity. The titration of Mohr salt resulted in a color change from orange to blue-green and the clockwise of the electrode moved upward and stopped. Then, recording the consumption of Mohr salt. Three blank samples of dichromate solution ($K_2Cr_2O_7$) were determined for factor to calculation the SOC content.

The SOC content was calculated as a percentage (%) using the following equation:

$$C_{org} = (12 - 0.3 * S * f) * 100 / N$$

- **f** is the dichromate factor (f = 40/a)
- **a** means the consumption for blank sample titration (mL)
- **S** is consumption for titration of the samples (mL)
- **N** is the sample weight (mg)

3.3.4. Thermal gradient with continue heating

The thermal gradient with continuing heating up to 900°C and with a soliTOC cube (elementar, Lanenselbold, Germany) was used for evaluation of the stability and quality of SOM, according to Rennert and Herrmann (2022). The milled soil samples were weighed 20 or 50 mg (depending on the organic carbon contained in the soil) into the ceramic tube and placed into the SoliTOC elementar analyser (Elementar Analysensyteme). The standards (soil, $CaCO_3$, flour, lesin, a mixture of sand and flour) were prepared for calibration and calculation. At a heat rate of 70 K min^{-1}, the weighed soil samples were heated to 450 °C (and the temperature was held constant for 500 s), then to 600 °C (temperature constant for 450 s), and finally to 900 °C (temperature constant for 150 s). An infrared detector quantified the CO_2 evolved in each temperature interval. The CO_2 detected at T = 20–450 °C (C-450) and T = 451–600 °C (C-600) to organic C, and that detected at 601–900 °C (C-900) to inorganic C.

3.3.5. Humic and fulvic acids extraction

Humic (HA) and fulvic (FA) acids were extracted from sieved soil samples under different depths and land uses. It was determined according to the International Humic Substance Society (IHSS) fraction method modified by Piccolo et al. (2000) (Figure 12). Sixty grams of soil were extracted by adding 300 ml of a mixture of 0.5M NaOH and 0.1M $Na_4P_2O_7$ and then shaking them for 24 h. The suspension was centrifuged at 4000 rpm for 15 minutes and then supernatant was transferred into beakers. This procedure was repeated three times. The supernatant was acidified to pH 1.0 using HCl and left overnight in the refrigerator for precipitation and separation of humic substances into humic and fulvic acids. The HA was dissolved with 1M NaOH and precipitated with HCl. To purify the co-extracted clay, the precipitated HA was added a 300 ml of mixture solution of 0.5% HCl and 0.5% HF (v/v) and then shaken for 2 days. The HA suspension was centrifuged at 4000 rpm for 10 min and neutralized. The supernatant containing HA was then transferred into a dialysis bag and soaked it with distilled water in a cylinder to free chlorine. HA was frozen and freeze-dried. The fulvic acid (FA) was purified using hydrophobic resin in the column. The solution of 0.5M NaOH was used for unbinding FA sorption in resin. Finally, the FA was neutralized and then dialyzed. The following steps were the same as the HA procedure.
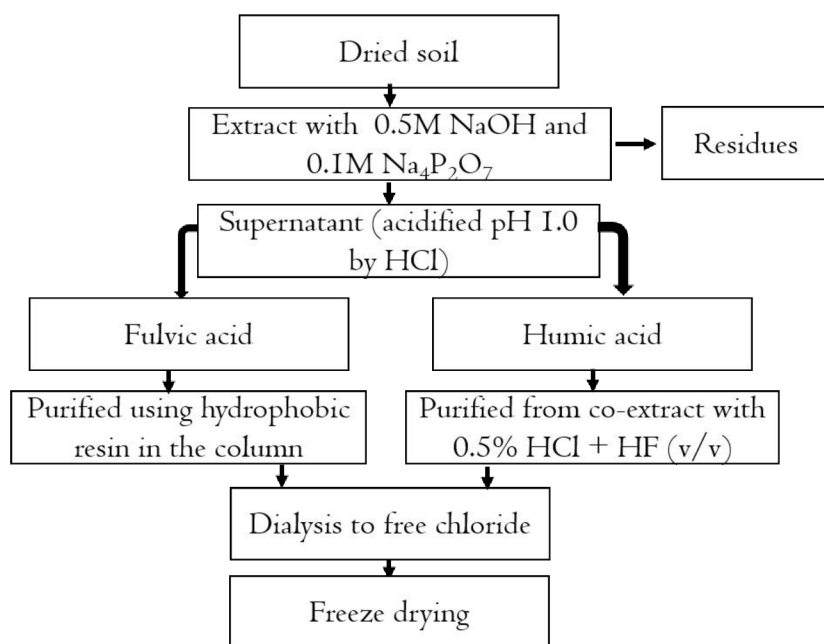
Figure 12. The extraction procedure of humic and fulvic acids.

3.3.6. DRIFT spectroscopy

DRIFT spectra of pure freeze-dried humic acids, fulvic acid, and finely milled soil samples were recorded by the infrared spectrometer (Nicolet iS10, Waltham, USA). Due to the lightness and darkness of soil samples, the spectra were recorded at 64 scans (light samples) and 120 scans (dark samples) in wavenumbers ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm−1. The gold mirror was used as a background reference. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., Waltham, USA) was applied for spectra analysis. Kubelka-Munk units were employed to assess the qualitative characteristic of SOM and to calculate some indices such as potential wettability index (PWI), aromaticity index (iAR), and decomposition index (iDEC).

The potential wettability index (PWI) was designed according to the adsorption band of the alkyl C-H groups – A (2948-2920 cm^{-1}), indicating the relative hydrophobicity and adsorption band of the C=O groups - B (1740-1698 and 1640-1600 cm^{-1}), which ascribed to hydrophilicity. PWI was calculated as a ratio by summing up the intensity of the C-H and C=O groups (Ellerbrock et al., 2005).

$$PWI = A/B$$

The aromaticity index was calculated according to the reflectance of aliphatic bands ranging from 3000-2800 cm^{-1} (I_{AL}) and the aromatic band at 1520 cm^{-1} (I_{AR}) (Cunha et al. 2009).

The aromaticity index (i_{AR}) was calculated as follows:

$$i_{AR} = I_{AL}/I_{AL}+I_{AR}$$

- I_{AL}: Intensity of aliphatic bands
- I_{AR}: Intensity of aromatic bands

The index of decomposition (iDEC) was based on the absorption band at 1640-1600 cm^{-1} (X) and 1030 cm^{-1} (Y). The iDEC was calculated by summing up the intensities of the C=O group band and polysaccharide band intensity and then performed as their ratio (Artz et al., 2006).

$$iDEC = X/Y$$

3.4. Data analysis

The software IBM SPSS (version 26, New York, USA) was used to analyze the data. To run the data correctly, the homogeneity of variances was applied to check its normality. The comparison of soil chemical characteristics among land uses, years, and soil horizons was statistically analyzed using ANOVA at an error level of 0.05 (confidence level of 95%). T-test was assessed to determine the difference between the forest species (beech and spruce). The statistical differences among depths, land uses, and between forest types were presented in alphabetical letters, using the Tukey test. A correlation matrix among the chemical properties was also performed. Linear regressions models were also used for prediction of soil properties from diffuse infrared reflectance spectra. Principal analysis (PCA) was used to access co-variations and evaluate the relationships between the chemical compositions using the R studio program (Girona-García et al., 2018).

4. Result and discussion

4.1. Comparison of SOM composition under different land use

The composition of SOM generally varies under different vegetation cover and through the soil profiles. Our first study aimed to evaluate the SOM composition across different land uses, including cropland, grassland, and forest land at various soil depths. The result found that the most significant differences in the soil spectra in the composition of SOM occurred in the upper parts of the soil profiles. The forest soil exhibited more in aliphatic CH groups than the grassland and cropland in the upper layer. This indicates the living and dead plant matter accumulating in the uppermost layers in forest soil (Habumugisha et al. 2018; Langenbruch et al. 2012; Galka et al. 2014). Similarly, the HA spectra (Figure 13) of forest soil had more intense aliphatic bands than the HA spectra of grassland and cropland, indicating the intensive decomposition of aliphatic in SOM of cropland due to soil disturbance from tillage through the soil profile (Pospíšilová et al., 2011; Ranjan et al., 2017; Pavlů et al., 2021). In addition, the result found that the aromaticity under cropland increased with depth. Our finding also showed that the concentration of DOC and LMMOA was relatively higher in forest soil, followed by grassland and cropland. This indicates the attributing of plant root exudation, residues, litter decomposition and microbial activities as highlighted by Adeleke et al. (2017), Berg and McClaugherty (2020), and Hubová et al. (2017).
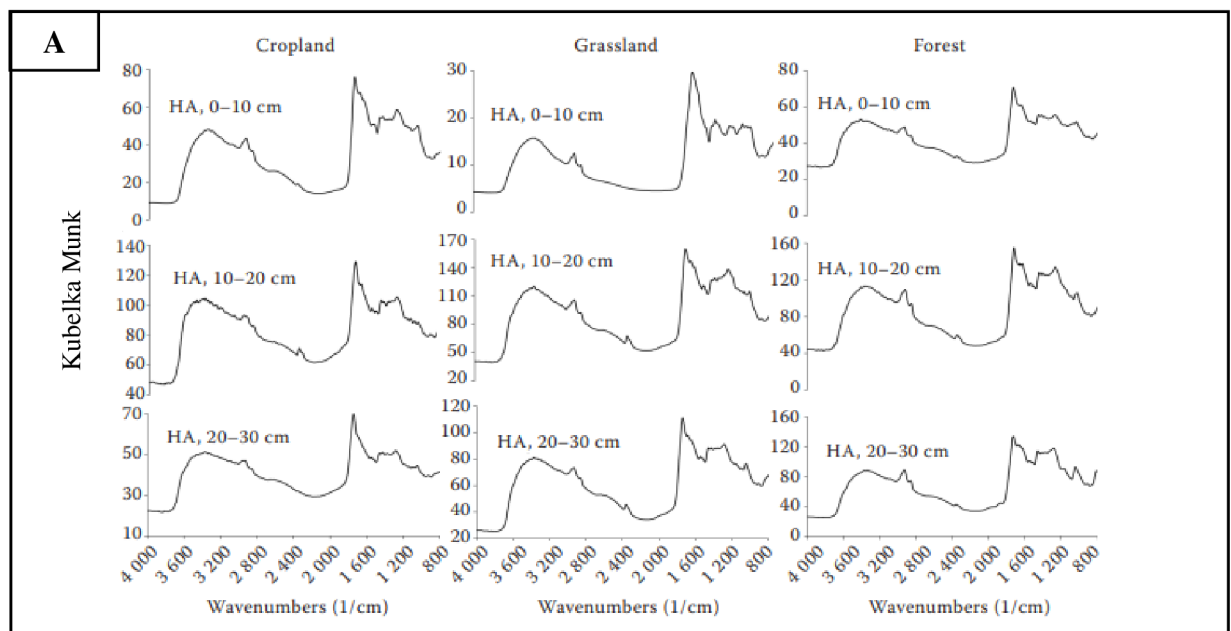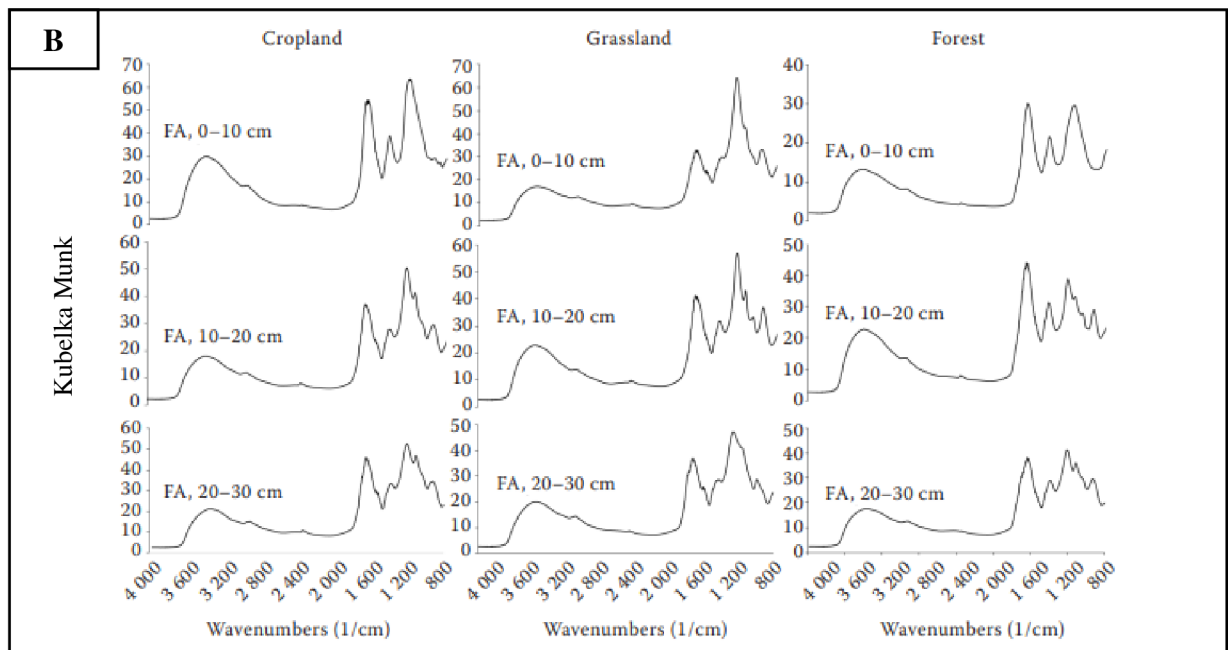
Figure 13. (A) The average spectra of humic acid (HA) and (B) fulvic acid (FA) under different depths and land uses.

Liu et al. (2006) reported that agricultural practices, such as tillage, fertilizing, irrigation etc., are the main factors affect the soil aggregates, water holding capacity, infiltration, and the decomposition rate, and adversely affect the SOM stabilization. Therefore, changes in agricultural practices by reducing tillage, changing from monoculture to crop rotation, and especially application of organic mulches can increase the soil nutrients, maintained the soil temperature, restricted water evaporation, and soil SOM stabilization (Ranjan et al., 2017; Pavlů et al., 2021).

4.2. SOM interaction with mineral phase of soils

In our research, we also investigated the influences of application of different organic mulches on soil aggregate stability. The result found that after the application of organic mulches, such as straw, wood chips, and bark chips, the organic carbon content within aggregates was higher compared to that in the bulk soil. This phenomenon suggests that carbon was effectively stabilized within the aggregates and sequestered in the soil (Six et al. 2004; Tivet et al. 2013; Goebel et al. 2005). Notably, among the mulched soils, wood and bark chips exhibited higher organic carbon content than straw, likely due to the quality of the organic matter (Luna et al. 2016). Additionally, the evaluation using infrared spectroscopy showed the aggregate spectra of all soils including control treatment had higher reflectance of the secondary alumosilicates than the bulk soil spectra. This indicates that these minerals abundant in clay fraction play an important role in aggregate creation, but the differences

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in aggregate stability are mainly affected by organic compounds (Haas et al. 2018; Six et al. 2004). However, the study found a higher proportion of aliphatic components in stable aggregates than in unstable aggregates from the control plot. This can indicate the high SOC content with high hydrophobicity, which lowered soil wettability and reduced the infiltration rate (Goebel et al. 2005) and are able to protect the aggregate from dispersion with water (Hallett & Young 1999). It is a similar finding to our third article showing that the higher SOC content under beech can reduce the soil wettability. The effect of SOC on soil wettability had several mechanisms. The hydrophobicity decreased wettability by reducing the surface free energy of the soil, restrict the soil from wetting (Turski et al. 2022) and decreased the rehydration rate (Eynard et al. 2004). However, the SOC improved the soil porosity by holding soil particles together against external disturbances (Eynard et al. 2004). It can be said that SOM can reduce soil wettability and lower wettability can prevent SOC from microbial decomposition (Atanassova et al. 2018; Ellerbrock & Gerke, 2013).

We also found that qualitative parameters of long term stabilized SOM depend on soil type or mineral phase of soils. Stability and resistance of organic matter is based on organic matter chemical composition (e.g. in Chernozems, SOM is more aromatic and relatively resistant to decomposition) but also (and probably mainly) on organic matter interactions with soil minerals. SOM is stabilized by two mechanisms: by the formation of mineral-associated organic matter and by the formation of aggregates (Angst et al., 2021). Higher proportion of aliphatic groups in the stable soil aggregates was discussed higher and in Thai et al. (2022). Polysaccharides and proteins as aliphatic components of SOM with affinity to organo-metallic complexes formation was described by Angst et al. (2021). Thus, it is possible that the stabilization of otherwise relatively mobile or easily decomposable organic matter in for example Cambisols is caused by binding to iron oxyhydroxides. Positive effect of iron forms on aggregates stability was found by Pavlů et al. (2022) exactly in this region.

4.3. Forest soil profile specifics and effect of tree species on SOM

The study had further observation of the soil chemistry and the composition of SOM and their transformation into the deeper soil horizons under different forest species (beech and spruce) and different soil types like Cambisols and Podzols. The study found that the content of SOC decreased through soil horizons (F > H > A > B) under both forest tree species. After a decade of observation, beech forest exhibits higher SOC content than spruce one in study locality. Additionally, we found that the SOM under beech contains more aliphatic components compared to SOM under spruce. A higher concentration of SOC and aliphatic CH group under beech than in spruce was not usually

found. Numerous studies confirmed that spruce promoted more organic carbon and higher thickness layer of organic horizons in a long-term observation due to the higher recalcitrant substances (e.g., lignin, resin, waxes, and phenolic compounds), which were difficult to be decomposed by microorganisms (Andivia et al. 2016; Grüneberg et al. 2019). It was similar to our finding in the second article that organic mulches containing more lignin like bark and wood chips promote more SOC compared to other organic mulches like straw. The contrast finding may result from the local environmental conditions and different forest stands such as age, density, and canopy forest (Yuan et al. 2013). Bradová et al. (2015), who studied the same locality, reported that the beech forest was older than spruce, by approximately 80 years, and had larger canopy closure (87%) than spruce (40%). The higher density and age of the forest stands in the research area had typically larger basal area of trees, in which it enhanced SOC in the forest soil (Menyailo et al. 2022). It was consistent with the finding of Yuan et al. (2013) who found that SOC was stored higher under the old-growth forest trees. The larger canopy of the beech forest stands, however, reduced the decomposition rate, while an open canopy led to SOC loss due to more favorable soil microclimates, higher exposure to throughfall, and warmer conditions, which accelerated the decomposition, leaching, and soil respiration by microorganism (Zech et al. 1996; Merabtene et al. 2021; Hanakova-Becvarova et al. 2022; Jandl et al. 2022). Climatic conditions, on the other hand, could alter the microbial activities and low molecular weight fractions to be more depolymerized by products under spruce and could be easily lost and transported into deeper soil horizons or leach into the groundwater (Lal 2008; Jamroz and Jerzykiewicz 2022; Zosso et al. 2023).

Our study also extended evaluation on SOM by focusing on the spectroscopic characterization of alkaline extractable organic substances (AEOS) extracted from the soil profile under beech and spruce forests. The low soluble AEOS (soluble only in alkaline nature and in mineral horizons called humic acids (HA)) and soluble AEOS (soluble in whole pH scale and in mineral horizons called fulvic acids (FA)). The result shows that the aliphatic CH groups within soluble AEOS gradually disappeared with deeper soil horizons under both forest species shown in Figure 14. This indicated the preferential biological degradation of carbohydrates, which are the main parts of the O-Alky C fraction (López et al. 2008). Whereas the aliphatic CH groups within low soluble AEOS were more pronounced in A horizon under spruce and relatively increased with depth under beech stands. This result could be explained by the fact that the amount of aliphatic groups within low soluble AEOS increased during decomposition and the formation of the micelles of low soluble AEOS (Sierra et al. 2005). The carboxylic groups were more prevalent in deeper soil horizons, while polysaccharide chains, as well as nitrogen functional groups, decreased with depths under both forest stands but were more prevalent

under beech than spruce stands. This indicated that the C=O stretch of COOH and ketones were present in deeper soil profiles and resulted from the oxidative cleavage of lignin side-chain and aromatic rings during the degradation (López et al. 2008). A higher abundance of DOC in F and H horizons (Figure 14) was an indicator of carboxylic groups becoming more soluble and transported into deeper soil horizons. The aromatic C=C stretching within low soluble and soluble AOES increased with depth under beech, while spruce stands were relatively constant through the soil horizons (Figure 14). Additionally, the fourth published article also found that the aromaticity of SOM increased with depth under different soil types. The similar finding were also reported by Tatzber et al. (2007), Zech et al. (1989) and Silva et al. (2022), showing that the aromaticity increased from L to B horizons. It was contrast to the finding of Ohno et al. (2014) where the abundance of condensed aromaticity of SOM was much lower in subsoil under coniferous and deciduous forests due to the adsorption of aromatic compounds to the minerals present in the soil profiles. The decrease or increase of the aromatic components through the soil profile, generally, depend on the association of plant residue compositions, climate conditions, soil types, soil history, and microorganism present in the soil (Koutika et al. 2020; Thai et al. 2022). The lower aromaticity in the uppermost soil layer (L and F horizons) than in the deeper soil profile under both forest tree species, however, was indicated by the less humified and decomposed organic matter due to the chemical and physical interaction mechanisms (Chen et al. 2013; Corvasce et al. 2006). Ussiri et al. (2003) found that the decomposition of forest residues relatively affected the aromaticity changes through the soil horizons. Nonetheless, the aromaticity in the soil profile had been shown to increase with degrees of decomposition and maturity of OM (Chefetz et al. 1998; Margenot et al. 2015; Veum et al. 2014). Aromatic compounds were less susceptible to becoming mobile, therefore, they are likely retained in the mineral soil horizon (Bi et al. 2013). The gradual disappearance of N-H bending and C=N stretching and polysaccharide chains with depth under both forest stands (Figure 14) can be interpreted that the N and polysaccharides being decomposed by soil microorganisms and could result from degradation of various moieties of forest litter substances from L to B horizons (Haberhauer et al. 1998; Leinweber et al. 2001). It was also noticed that the N-H bending and C=N stretching in the beech forests was more pronounced in L and F horizons than in the spruce one. The results agreed with Mládková et al. (2006) that low soluble AEOS originating from the organic horizons under beech forests were relatively richer in nitrogen functional groups than substances originating from spruce stands. These findings could suggest that the stability of organic matter through the forest soil profiles increased due to transformation of various organic compounds from litter to more stable organic matter with higher amounts of lignin components to greater amounts of carboxylic groups and aromatic groups in deeper soil horizons. Furthermore, a higher proportion of mobile component of

soil organic matter and acidic COOH, together with lower pH and cation exchange capacity under spruce, result in leaching of nutrients, releasing risk elements into soil solution, and accelerating podsolization process. However, changes in vegetation cover caused changes in the qualitative composition of soil organic matter throughout the forest soil profile and had relevant consequences on fundamental soil function and services such as biogeochemical nutrient cycling and carbon stock.
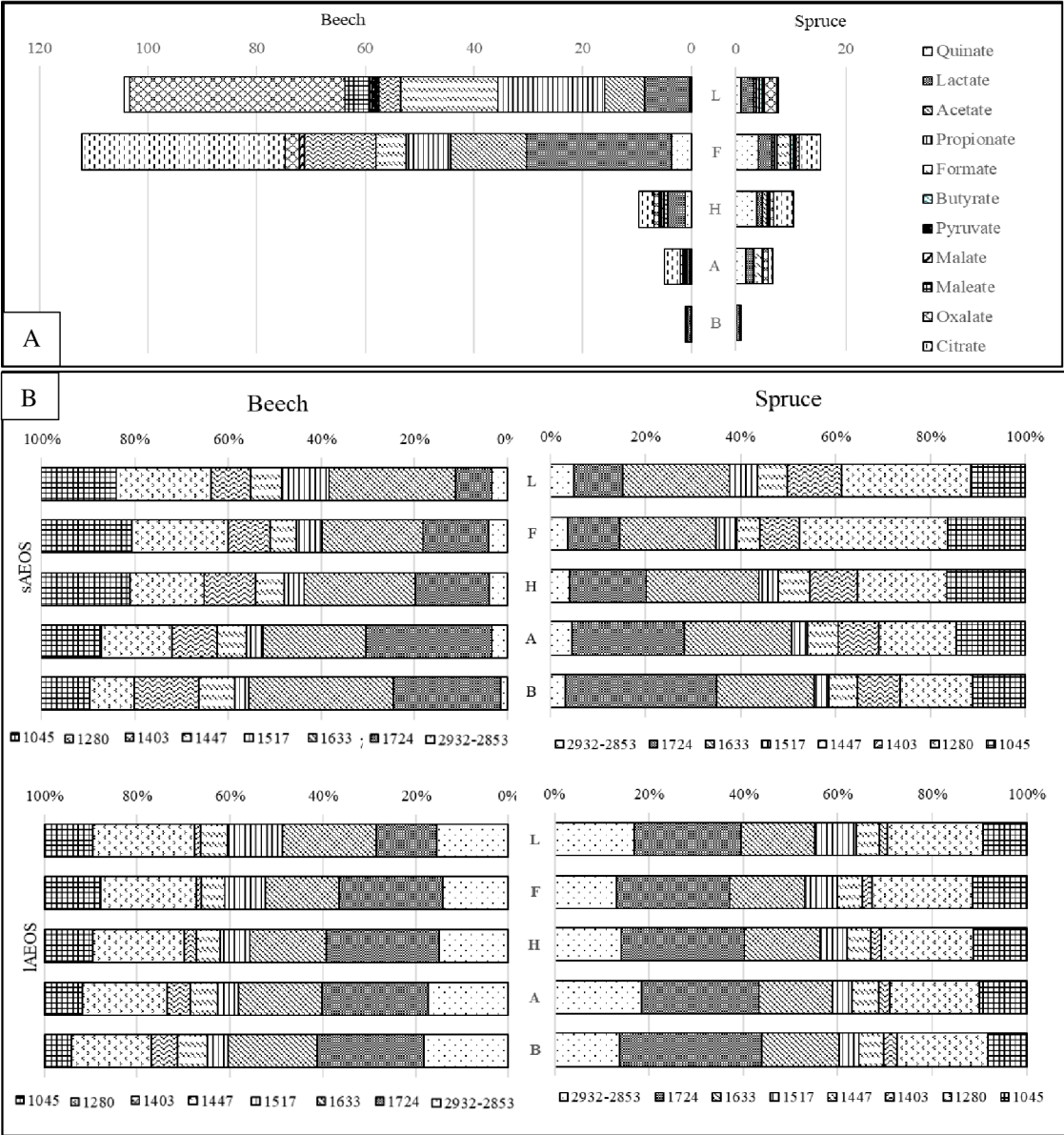

Figure 14. (A) The concentration of LMMOA expressed as mmol kg^{-1} and (B) the reflectance band of soluble alkaline extractable organic substances (sAEOS) and low soluble alkaline extractable organic substances (lAEOS) expressed as % in each horizon under beech and spruce forests.

5. Conclusion

The findings of this dissertation reveal that SOM and soil chemistry are influenced by vegetation covers, translocate chemical compositions differently through the soil profiles and soil types, even when they grow in the same or similar climate conditions, soil types, and elevations. Forest soil was found to have higher levels of aliphatic and carboxylic groups compared to grassland and cropland. However, the composition of SOM, including aliphatic, carboxylic groups, and polysaccharides, varied at different depths under all land uses. The aromatic group was more prevalent in deeper soil layers of cropland in comparison to forestland and grassland. This indicates higher plant residues, SOM and root exudation under forest, while SOM under cropland was rapidly mineralized due to agricultural activities, such as tillage and soil stirring.

The dissertation found that the stabilization of SOM within aggregates depends on the application of organic mulches on the soil. These organic mulches reduce the wettability of the aggregates, thereby protecting them from dispersion with water. On the other hand, it can be concluded that, in the long term, soil type (i.e., the set of climatic, geological, and geographical conditions) plays an important role in the stabilization and conservation of organic matter in the soil. Organic matter of Chernozems maintains a high proportion of aromatics and in contrast, the proportion of aliphatic components remains high in acid Cambisols even with a similar total C content.

Additionally, our study discovered that the temporal changes in chemical composition are influenced by several factors, including the quantity and quality of forest residues, as well as the surrounding environments such as climate conditions, age of the forest, canopy closure, and microbial activities. Besides that, my dissertation revealed that beech forests exhibit greater nutrient recycling, higher low molecular mass organic acids, and more dissolved organic carbon compared to spruce forests due to the presence of decomposable materials and biological activities. Moreover, after the natural beech forest was clear-cut and transformed into a spruce monoculture, the soil chemistry and SOM were visible in both organic and mineral horizons, changed and developed podsolization.

The study also demonstrates that DRIFT spectroscopy is a useful tool for identifying the composition and decomposition of SOM at different stages. Additionally, it could be used to determine the indices of aromaticity, and wettability within the soil, as well as the prediction as an indicator for SOM quality.

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7. Published papers

7.1. Comparison of soil organic matter composition under different land uses by DRIFT spectroscopy

Thai, S., Pavlů, L., Tejnecký, V., Vokurková, P., Nozari, S., Borůvka, L. (2021). Comparison of soil organic matter composition under different land uses by DRIFT spectroscopy. Plant, Soil and Environment. 67(5), 255–263.

https://doi.org/10.17221/11/2021-PSE

7.2. Causes clarification of the soil aggregates stability on mulched soil

Thai, S., Davídek, T., Pavlů, L. (2022). Causes clarification of the soil aggregates stability on mulched soil. Soil and Water Research. 17(2), 91–99.

https://doi.org/10.17221/151/2021-SWR

7.3. Temporal changes in soil chemical compositions in acidified mountain forest soils of Czech Republic

Thai, S., Pavlů, L., Tejnecký, V., Chovancová, S., Hin, L., Thet, B., Drábek, O. (2023). Temporal changes in soil chemical compositions in acidified mountain forest soils of Czech Republic. European Journal of Forest Research. 142, 883–897.

https://doi.org/10.1007/s10342-023-01564-x

7.4. Prediction of the distribution of soil properties in deep Colluvisols in different pedogeographic regions (Czech Republic) using diffuse reflectance infrared spectroscopy.

Pavlů, L., Zádorová, T., Pavlů, J., Tejnecký, V., Drábek, O., Rojas, J, Thai, S., R., Penížek, V. (2023). Prediction of the distribution of soil properties in deep Colluvisols in different pedogeographic regions (Czech Republic) using diffuse reflectance infrared spectroscopy. Soil and Tillage Research. 234, 105844.

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7.5. Changes in the composition of soil organic matter after the transformation of a natural beech stand into a spruce monoculture. (Under review)

Thai, S., Pavlů, L., Vokurková, P., Thet, B., Drábek, O., Vejvodová, K., Tejnecký, V. (2024). Changes in the composition of soil organic matter after the transformation of a natural beech stand into a spruce monoculture. Journal of Soil and Water Conservation (under review).

My contribution to each paper is 7.1 (80 %), 7.2 (60%), 7.3 (60%), 7.4 (5%), and 7.5 (80%).

7.1. Comparison of soil organic matter composition under different land uses by DRIFT spectroscopy

Thai, S., Pavlů, L., Tejnecký, V., Vokurková, P., Nozari, S., Borůvka, L. (2021). Comparison of soil organic matter composition under different land uses by DRIFT spectroscopy. Plant, Soil and Environment. 67(5), 255–263.https://doi.org/10.17221/11/2021-PSE

Comparison of soil organic matter composition under different land uses by DRIFT spectroscopy

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Abstract: The study aimed to estimate and characterise soil organic matter under different land uses (cropland, grassland, and forest) and soil depths. The soil organic matter composition of the soil was assessed by diffuse reflectance infrared spectroscopy (DRIFT). Humic and fulvic acids (HAs, FAs) were extracted from soils and their compositions were evaluated by DRIFT. Low molecular mass organic acids content was also measured. Our result revealed that the largest differences of the spectra in the composition of organic matter were observed in the upper parts of the soil profile. The forest soil spectra had more intense aliphatic bands, carboxylic, and CH bands than spectra of grassland and cropland soils. The difference of HAs spectra was at 3 010 to 2 800/cm where the most intensive aliphatic bands were in forest soil HAs, followed by grassland and cropland soil HAs. The grassland topsoil FAs spectrum differs most from the other land uses. It has lower peaks around 1 660–1 600/cm and 1 200/cm than cropland and forest. The concentration of low molecular mass organic acid (LMMOA) was the highest in the forest soil and the most abundant acid was citrate.

Keywords: terrestrial ecosystem; Luvisols; humus; organic compounds; functional groups

Soil organic matter (SOM) plays an important role in biological, chemical, and physical soil improvement and productivity (Strosser 2010). The living biomass including microorganisms breaks down the plant residues or detritus and animal waste into humus or organic matter by using carbon as an energy source and nitrogen as a source of protein production (Allison et al. 2007). The decomposition of plant residues releases the organic chemical compounds and helps to cling together with the mineral soil particles that improve the chemical soil properties by soil sorption complex creating and physical soil properties by establishing of soil structure (Davidson and Ackerman 1993).

However, SOM in the ecosystem has been stored in different layers with different concentrations as a result of different stages of decomposition (Ribeiro et al. 2001). The quantity and the quality of SOM depend on several factors such as duration of decomposition, residues, roots, amount of fine materials, type of decomposers (microorganisms), chemical composition, and temperature (Lal 2018). On the other hand, the fluctuation of the organic matter concentration in the soil is related intensively to slopes, elevation, topography, soil types, and land uses and management (Slepetiene and Slepetys 2005, Jakšík 2015). The humic substances such as humic acids (HAs) and fulvic acids (FAs) are also the component used to identify the quality of SOM. They play an important role in the terrestrial ecosystem (Trevisan et al. 2010), and they are known as a mixture of substances in the form of supramolecular

structures (Piccolo 2001). Humic substances make up about 20% of the total of SOM and result from the decomposition and humification process of the SOM (Pavlů and Mühlhanselová 2017). They are often understood as relatively stable components of SOM, which are involved in the fixation and sequestration of carbon in the soil (Lal 2005). The low molecular mass organic acid (LMMOA), which makes up about 10% of dissolved organic carbon (DOC), also characterises the compositions of soil organic matter. They are carboxylic acids of low molecular weight (Ash et al. 2016) and could be aromatic or aliphatic (Hubová et al. 2017). LMMOA are understood as relatively variable and unstable components of SOM (Strobel 2001).

Diffuse reflectance infrared fourier transform spectroscopy (DRIFT), as one of the types of infrared spectroscopy conventionally used for solid powder samples, is commonly used to analyse peat soil, composts, and the transformation of organic matter during composting within various stages (Haberhauer and Gerzabek 1999, Zaccheo et al. 2002, Pavlů and Mühlhanselová 2017). The DRIFT spectra have been recognised as one of the spectroscopic techniques used to distinguish the fluctuation in the abundance of organic functional groups during decomposition and to identify the changes of SOM in the soil profile under different vegetation covers (Veum et al. 2014).

The study hypothesised that different land uses are connected with different incoming fresh organic materials and these differences can be seen throughout the whole soil in the composition of organic matter. Therefore, the study aimed to describe and compare the SOM compositions and their transformation under different depths and vegetation covers. The comparison of the separated organic compounds such as humic and fulvic acid and low molecular mass organic acid was observed by the combination of the advanced analytical methods.

MATERIAL AND METHODS

Site selection and soil sampling. The research was conducted on the outskirts of Prague, Suchdol (Czech Republic). The area is situated in altitude range 250–300 m a.s.l. and has a mean annual precipitation of about 470 mm and a mean average temperature of 11 °C. The mixture of loess and sandy river sediments of the Quaternary age creates the bedrock of the research area. Haplic Luvisols are the prevailing soil type in all land uses. Cropland site (with

a dominantly grown wheat (*Triticum aestivum* L.) crop interspersed with rape (*Brassica napus* L.) and maize (*Zea mays* L.)) marginally include the areas of greyic Phaeozems and carbonates were detected in several soil samples mainly in deeper layers. Soil texture belongs to clay loam category. Same soil description applies to grassland site (poorly maintained grassland with *Dactylis polygama* Horv., *Poa annua* L., *Calamagrostis epigejos* Roth). Broadleaf forest site with the dominant abundance of oak (*Quercus petraea* (Matt.) Liebl.) followed with beech (*Fagus sylvatica* L.) and hornbeam (*Carpinus betulus* L.) marginally include the areas of Regosols and Cambisols. The presence of carbonate was not detected in all soil samples from the forest. Soil texture belongs to sandy clay loam category.

Ninety soil samples were collected from each land uses and categorised for the three different depths (0–10 cm (with exclusion of litter layer in forest), 10–20 cm and 20–30 cm). In all cases, the samples from the first two layers captured humic (A) horizon. Samples from the deepest layer captured either still horizon A (in the case of Phaeozems or its gradual transformation to eluvial horizon in case of Luvisols, to cambic horizon in Cambisols or to mineral substrate in Regosols.

The taken samples were air-dried and sieved with a 2 mm sieve. Furthermore, 2-mm-sieved soil samples were milled (Fritsch Analysette 3 Spartan Pulvensette miller, Idar-Oberstein, Germany) into very fine particles to use for infrared spectroscopy. Fulvic and humic acid were extracted from selected 18 soil samples. The fresh topsoil (15 soil samples) was taken separately and frozen for analysing the DOC and LMMOA.

Soil analysis. The exchangeable (pH_{KCl}) was determined potentiometrically by the pH-electrode SenTix 21 (Inolab pH level 21, WTW, Prague, Czech Republic). Soil organic carbon (SOC) was measured by using rapid dichromate oxidation techniques (Sparks 1996). The quality of humus was determined by the absorbance ratio of sodium pyrophosphate ($Na_4P_2O_7$) soil extract at 400 nm and 600 nm (E4/E6, respectively) (Sparks 1996). The content of LMMOA was measured using ion chromatography (IC) with suppressed conductivity (Hubová et al. 2017). Dissolved organic carbon content was measured by the wet dichromate oxidation method according to Tejnecký et al. (2014).

The extraction of humic substances was carried out by the international humic substance society (IHSS)

Table 1. Describing the soil characteristic among the different depths (0–10, 10–20 and 20–30 cm)

	Depth (cm)	pH_{KCl}	Humus quality index	Soil organic carbon (%)
Cropland	0–10	6.79 ± 0.37	3.27 ± 0.37	1.37 ± 0.17[a]
	10–20	6.76 ± 0.33	3.25 ± 0.34	1.41 ± 0.20[a]
	20–30	6.85 ± 0.43	3.24 ± 0.43	1.11 ± 0.13[b]
P-value		0.852	0.977	0.001
Grassland	0–10	5.93 ± 0.19	3.50 ± 0.36	2.11 ± 0.31[a]
	10–20	5.73 ± 0.79	3.30 ± 0.17	1.58 ± 0.25[b]
	20–30	5.91 ± 0.70	3.28 ± 0.20	1.51 ± 0.38[b]
P-value		0.788	0.149	0.000
Forest	0–10	3.59 ± 0.21	4.41 ± 0.43	5.64 ± 2.54[a]
	10–20	3.52 ± 0.13	4.56 ± 0.42	1.78 ± 0.49[b]
	20–30	3.65 ± 0.10	5.02 ± 1.17	1.06 ± 0.34[b]
P-value		0.206	0.195	0.000

Data (means ± standard deviation; *n* = 10)

fraction method, which is modified by Piccolo et al. (2000). A mixture of NaOH and $Na_4P_2O_7$ was used to extract the humic substances. The extract was acidified to pH 1.0 using HCl for precipitation of humic acids and their separation from fulvic acids. The HAs fractions were purified by redissolution with NaOH and reprecipitation with HCl. The purification from co-extracted clay was completed with the solution of HCl and of HF. The suspension was neutralised, centrifuged, and dialysed to release chlorine and then the HAs were freeze-dried. The FAs solutions were purified using the hydrophobic resin in the column. The FAs were released from the sorption of resin using NaOH solution. Finally, the FAs were neutralised, dialysed, and freeze-dried.

DRIFT spectra of pure freeze-dried humic acids, fulvic acid, and dried fine soil samples were recorded by the infrared spectrometer (Nicolet iS10, Waltham, USA). The spectra with a range of 2.5 to 25 μm (4 000 to 400/cm) were used. The gold mirror was used as a background reference. The 64 scans with resolution 4/cm and Kubelka-Munk units were applied. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., Waltham, USA) was applied for spectra analysis.

Data analysis method. The software IBM SPSS (version 26, New York, USA) was used for data analysing and One-way ANOVA was applied for determining the statistical differences among quantitative soil characteristics with different land uses, and depths at significance level description $P < 0.05$. Tukey test and letters a, b, c were used to describe the significant differences, where a is the highest value, followed by b and c.

RESULT AND DISCUSSION

Basic soil characteristics. The analysed data (Tables 1 and 2) indicated that there are no significant differences for the pH_{KCl} among all three depths in all land uses. However, the soil in crop-

Table 2. The differences description of basic soil characteristics among the three land uses (cropland, grassland, and forest)

	pH_{KCl}			E4/E6			Soil organic carbon		
	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
	(cm)								
Cropland	a	a	a	b	b	b	b	ns	b
Grassland	b	b	b	b	b	b	b	ns	b
Forest	c	c	c	a	a	a	a	ns	a
P-value	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.067	0.000

Letters indicate significant difference; ns – none significance; E4/E6 – the humus quality index

land is neutral, in grassland is moderately acidic while in forest is strongly acid. Similarly, the method used for the indicative evaluation of SOM quality (E4/E6) in different depths in all the land uses had no significant differences. The cropland and grassland have very good humus quality while the forest does not. The higher E4/E6 ratio in forest could indicate lower degree of humification processes (Kunlanit et al. 2019). Soil organic carbon content is significantly different among the three depths of all land uses. Table 2 shows in the depth 0–10 cm, the SOC has the highest content in the forest, followed by the grassland and cropland. For the 20–30 cm depth, the grassland has the highest SOC comparing to SOC in the cropland and forest. Various studies found the same result, that grassland had higher SOC than cropland and forest in deeper soil layers (Muktar et al. 2018).

DRIFT spectra

Spectra of soils. Position and identification of soil spectra bands are presented in Table 3. The spectra of the cropland soil are very similar in all sampled depths (Figure 1). This corresponds well to tillage and soil stirring. In the soil spectra of the different depths under the grassland, there are also no differences in bands position, intensities, or shapes. The forest soil spectra of 0–10 cm layer differ from the

two deeper layers. The higher content of aliphatic components is evident from band absorbance in the range between 3 000–2 800/cm.

The most obvious differences among land uses are visible in soil spectra of the surface layer. The spectrum of forest soil differs from others. The bands of aliphatic groups are well identifiable between 3 000 and 2 800/cm. The extension of the band with a maximum from around 1 660/cm to the region of the carboxyl group (1 720/cm) is apparent and the band shape differs between 1 500 and 1 200/cm (polyphenolic substances and functional groups with nitrogen and phosphorus). The band around 920/cm documents a lower content of secondary alumosilicates (apparent in the whole profile), which corresponds to more sandy soil texture in forest. Hence, a large proportion of aliphatic, carboxylic, aromatic, and CH groups under forest correspond with higher organic carbon content in this soil (Gerzabek et al. 2006).

In the deeper layers of forest soil, the shoulder of carboxyl groups in the band with a maximum around 1 640/cm is still visible. The dominant peak of the forest soil spectrum is the band around 1 300/cm. In the depth 20–30 cm, the band at 1 040–945/cm (indicating C-O stretching, Si-OH of alumino-silicate lattice, and carbohydrate region of polysaccharides) is lower under forest than grassland and cropland. The polysaccharides content decrease through the

Table 3. The assignment of the major bands in infrared spectra of the soil (Tinti et al. 2015, Matamala et al. 2017)

| Wavenumber (1/cm)	Assignment of sorption bands
3 600–3 700	Si-O-H vibration of clays
3 440–3 320	O-H and N-H stretching, H-bonded OH
3 010–2 800	aliphatic CH stretching
2 000–1 790	Si-O vibration of quartz mineral
1 775–1 711	C=O stretching in carboxylic group
1 691–1 642	C=O stretching of amides (amide I), H-bonded conjugated ketones, carboxyls and quinones, lignin, C=N stretching
1 642–1 569	amide II of primary amides, aromatic C=C, C=O (quinones), carboxylates
1 544–1 488	aromatic C=C stretching, aromatic skeletal vibration, aromatic (lignin), amide II
1 479–1 444	CH and NH of amide II, aliphatic CH deformation, carbonates
1 444–1 408	C-H deformation and C-O stretching of phenolic groups
1 403–1 354	C-O of phenolic OH, COO⁻ and O-H, CH_3 bending,
1 342–1 307	C-N (aromatic amines)
1 293–1 256	C-O of aryl ethers, C-O of phenols, C-O-C ether bond, bentonite
1 256–1 198	C-O stretching and OH deformation of COOH, C-O of aryl ethers and phenols, silicate
1 185–1 070	C-OH of aliphatic alcohols, O-Si-O stretching of quartz, sulfates
1 056–945	C-O stretching, polysaccharides, Si-OH of alumino-silicate lattice (kaolinite, illite)
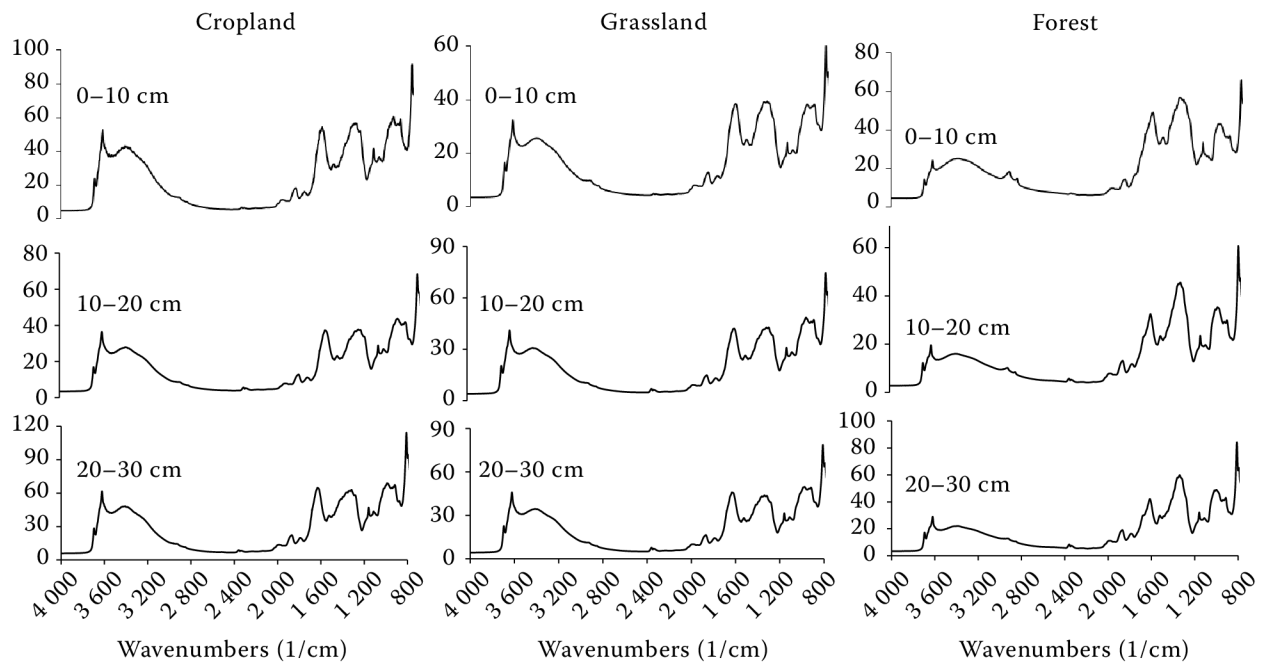
Figure 1. The difference of average soil spectra under different depths (0–10, 10–20 and 20–30 cm) and land uses (cropland, grassland, and forest)

depth of the forest soils was documented by Sugiura et al. (2017) and probable a higher appearance of inorganic materials (Haberhauer et al. 1998).

Spectra of humic acids. The main bands of HAs and FAs spectra are described in Table 4. The dominant peak of these spectra is a peak around 1 740/cm,
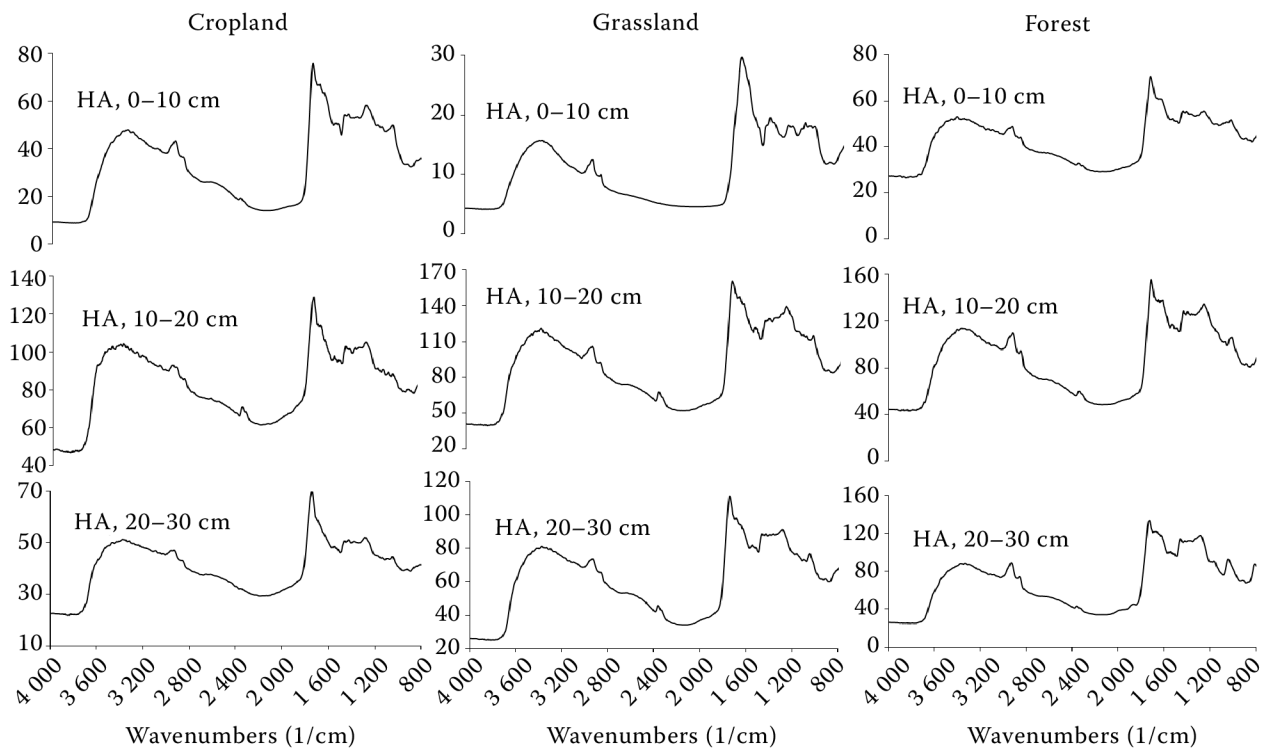

Figure 2. The difference of average humic acids spectra under different depths (0–10, 10–20 and 20–30 cm) and land covers (cropland, grassland, and forest). HA – humic acid

Table 4. The major bands of humic substances (humic and fulvic acids) in infrared spectra (Stevenson 1995, Tatzber et al. 2007, Pavlů and Mühlhanselová 2017)

Wavenumber (1/cm)	Assignment of sorption bands
3 400–3 300	O-H stretching, N-H stretching
2 950–2 800	aliphatic C-H stretching
1 725–1 710	C=O stretching of COOH and ketones
1 660–1 630	C=O stretching of amide I, quinone, H-bonded conjugated ketones
1 620–1 600	aromatic C=C stretching
1 590–1 517	N-H bending and C=N stretching (amide II)
1 470–1 380	aliphatic C-H bending
1 400–1 390	OH deformation of CH_2 and CH_3
1 280–1 200	C-O stretching and OH deformation of COOH, C-O stretching of aryl esters
1 170–950	C-O stretching of polysaccharides

which represents the carboxylic groups on aromatic rings (Figure 2). The vibration band of the carboxylic group is typically placed near 1 720/cm in the case of substitution on aliphatic chains. In case of substitution on aromatic rings is placed just near 1 740/cm (Reddy et al. 2018).

The surface layer of the cropland soil differs from deeper layers, more pronounced peak can be seen around 3 000–2 800/cm and 1 000/cm, which represents higher contents of aliphatic components and polysaccharides chains of HAs. It could point to their lower maturity and stability (Pavlů and Mühlhanselová 2017). The intensity of the C=O group of ketones and amide group (shoulder in range 1 690–1 630/cm) decreases with soil depth.

The spectrum of the surface layer of the grassland varies by the spectra from other depths and also from other land use. The band around 1 660/cm is dominant, while the carboxyl band is hidden in the spectrum, and the band around 1 280/cm is relatively less pronounced in comparison to other spectra. The aliphatic-bending at 1 460/cm is shifted to 1 425/cm in grassland HAs spectra of the surface soil layer, while in forest and cropland HAs spectra are clearly visible at both positions. It might be the formation of H-bonds between hydroxyl and carboxyl H atoms of HA (Senesi et al. 2001).

HAs spectra of deeper layers of forest soil, differ from others in pronounced aliphatic bands (3 000–2 800/cm). In addition, it could be connected with more sandy substrate in forest as described by Di et al. (2016). The forest HAs spectra have relatively (compared with neighboring band around 1 720/cm)
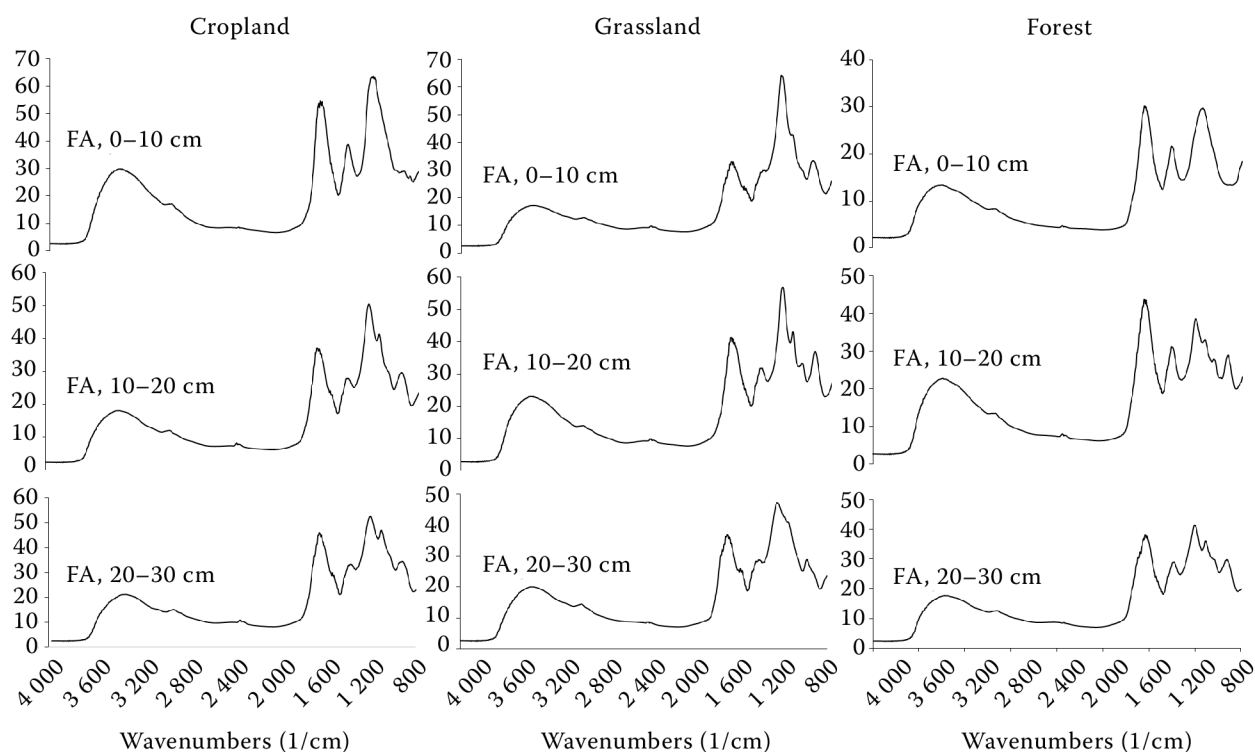

Figure 3. The difference of average fulvic acids spectra under different depths (0–10, 10–20 and 20–30 cm) and land uses (cropland, grassland, and forest). FA – fulvic acid
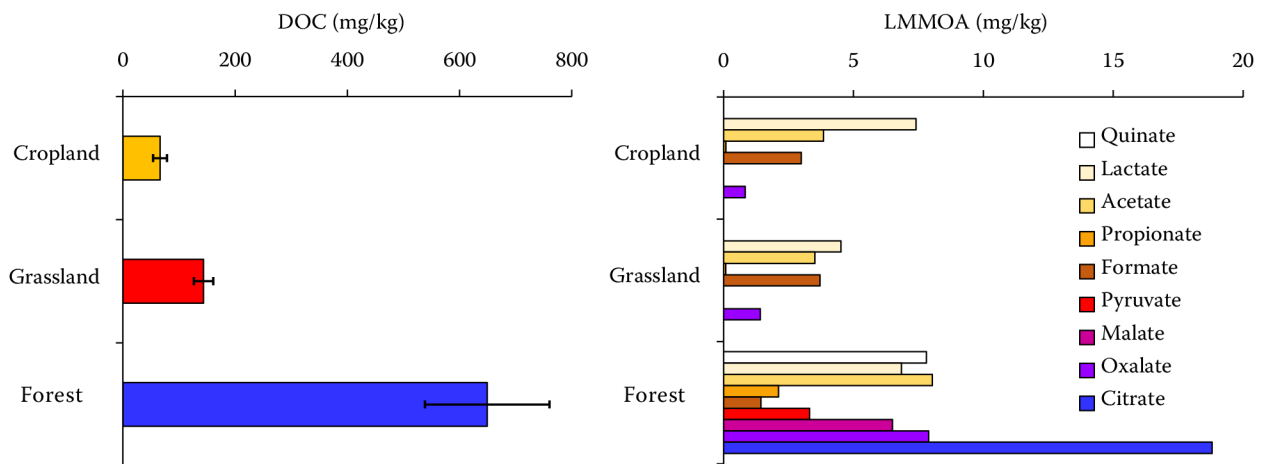
Figure 4. The mean concentrations of dissolved organic carbon (DOC) (error bars show standard deviations) and low molecular mass organic acid (LMMOA) under different land uses (*n* = 5)

the highest peak around 1 660/cm in comparison with other land use and soil depth below 10 cm. The band of aliphatic C-H (1 470–1 460/cm) is also higher under forest than the grassland and cropland.

Spectra of fulvic acids. Generally, the spectra of FAs have a lower amount of peaks in the fingerprint area (Figure 3). More details are visible in the spectra of lower parts of the soil profile, where bands of polysaccharide chains and deformation vibrations of OH groups in carboxyl appear.

The FAs spectra from different soil depths under cropland are quite different. The band at 1 670–1 600/cm, which mainly characterises carboxyl, ketones, and aromatics, is clearly visible in all three depths. However, the shoulder at 1 570–1 560/cm (COO- symmetric stretching, N-H deformation,

and amides group II) is more pronounced in the deeper layers. The band at 1 420–1 400/cm (phenols and alcohols) is sharp in the uppermost layer. The spectra of FAs from surface layer of grassland have a bigger amount of peaks in the fingerprint area. The relative intensity of the band 1 680–1 630/cm and 1 100–1 200/cm increase with depth. The grassland FAs spectrum differs most from the other land uses in the depth of 0–10 cm. It has significantly lower peaks around 1 660–1 600/cm and 1 200/cm than cropland and forest. The band at 1 560–1 510/cm is more intense under grassland than cropland and forest. Gerzabek et al. (2006) found that aromatic and NH groups were greater in grassland than arable land. The FAs spectra of the surface forest soil layer have only three wide peaks in the fingerprint area. In the

Table 5. The description of low molecular mass organic acid (LMMOA) and dissolved organic carbon (DOC) concentration under different land uses in the upper layer (0–10 cm); means ± standard deviation; *n* = 5

		Cropland	Grassland	Forest
LMMOA (mg/kg)	quinate	bdl	bdl	7.81 ± 8.13
	lactate	7.40 ± 6.26	4.52 ± 1.35	6.85 ± 1.57
	acetate	3.84 ± 2.34	3.51 ± 3.57	8.04 ± 11.89
	propionate	0.09 ± 0.05	0.08 ± 0.08	2.11 ± 1.67
	formate	2.99 ± 2.65	3.71 ± 3.89	1.44 ± 0.88
	pyruvate	bdl	bdl	3.31 ± 2.95
	malate	bdl	bdl	6.50 ± 5.77
	oxalate	0.83 ± 0.52	1.41 ± 0.69	7.89 ± 6.63
	citrate	bdl	bdl	18.8 ± 25.08
DOC (mg/kg)		66 ± 27.36	144 ± 38.55	649 ± 247.92

bdl – below determination limit

FAs spectra of a deeper layer are visible their splitting on several peaks. The forest FAs spectrum under the depth 10–20 cm has the opposite intensities ratio of bands (1 660 ≥ 1 200) to the other two land uses (1 660 ≤ 1 200). It means that the forest has a higher presence of quinone, ketones, and aromatic C=O than C-O and OH deformation of COOH. It is in accordance with the work of Leinweber et al. (2001).

Dissolved organic carbon and low molecular mass of organic acids. On the base of previous results, the most differences among land use are focused on top parts of the soil profile where LMMOA was mostly found (Hubová et al. 2017). The description of this part of the profile is therefore extended to DOC and LMMOA evaluation (Figure 4, Table 5).

The concentration of DOC is relatively high under forest, followed by grassland and cropland. Lower DOC in cropland may result from ploughing, drainage, intensive surface runoff, which cause DOC losses (Manninen et al. 2018). Forest was found to have the highest concentration of LMMOA (citrate, acetate, quinate, oxalate, malate, pyruvate, propionate, formate) followed by grassland and cropland. Citrate concentration is higher under forest while lactate concentration is higher under grassland and cropland. Hubová et al. (2017) showed that more acidic soil contains a higher concentration of citrate. The big value of standard deviation in LMMOA is natural for this slightly stable and highly variable component of soil organic matter. On the other hand, it has a correlation between the amount of LMMOA and DOC with *P*-value 0.01 ($r = 0.755^{**}$) under all land uses. The high concentration and amount of LMMOA are based on plant root exudation, residues, and litters decomposition reviewed by (Adeleke et al. 2017, Hubova et al. 2017), and the highest content in forest is as a result of litter decomposition (Berg and McClaugherty 2020) and lower pH in forest area (Rukshana et al. 2014).

It can be summarised that land uses influence the amount and qualitative parameters of soil organic matter. Infrared spectroscopy is a useful tool for composition of the SOM evaluation. The most obvious differences in SOM composition according to land use are evident in surface layer of soil. Forest soil spectra had more intense aliphatic bands (3 010–2 800/cm) than the grassland and cropland in the upper layer. Similarly, the HAs spectra of forest soil have more intense aliphatic bands than the grassland and cropland HAs. More acid characters of organic matter in forest soil are also documented by soil spectra in the intensity of carboxylic bands. The grassland FAs spectrum differs most from the other land uses in the depth of 0–10 cm. It has significantly lower peaks around 1 660–1 600/cm and 1 200/cm than cropland and forest. In the cropland soils, aromaticity of HAs increase with depth. The concentration of LMMOA was higher under the forest, followed by grassland and cropland. The most abundant acid in LMMOA mixture was citrate in the forest while lactate was in the grassland and cropland.

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7.2. Causes clarification of the soil aggregates stability on mulched soil

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Causes clarification of the soil aggregates stability on mulched soil

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Abstract: Soil aggregates have great effects on soil properties and soil functions. Mulching (organic inputs) has been known as a factor influencing soil aggregate stability. Our study aimed to reveal the causes of the higher stability of soil aggregates under organic mulches. The primary soil characteristics such as organic carbon (C_{ox}), humus quality (E4/E6), potential wettability index (PWI), and aromaticity index (iAR) were determined. The C_{ox} was measured using rapid dichromate oxidation, and E4/E6 was measured using the UV-Vis spectrophotometry. The PWI and iAR were determined according to the intensity of selected bands in diffuse reflectance infrared spectra. Results showed that mulched plots contained higher C_{ox} content in aggregates in comparison with whole soil. This indicates that the carbon was stabilized within the aggregates and sequestrated into the soil. The iAR was significantly higher after using the organic mulches, the aliphatic components of the organic matter thus contribute more to the aggregates stabilization. The PWI of aggregates was found to be higher after applying these mulches than in soil. Organic mulches are therefore able to reduce the wettability of the aggregates and also to protect the aggregate from dispersion with water.

Keywords: Haplic Fluvisol; infrared spectroscopy; organic compounds; soil structure

Soil aggregates are the fundamental core to regulate the soil properties (Wang et al. 2017). A stable aggregates produce favourable conditions for plant growth and soil quality improvement by maintaining the water infiltration, moisture content, nutrient cycle, and especially the C storage (Kumar et al. 2019). Soil aggregates are composed by binding the mineral and organic substances that came from the decomposition of organic matter. The formation of aggregates is developed on the base of various theoretical models. The vital theoretical models are the following: the hierarchical order of aggregates exist in the soil where soil organic matter (SOM) is the major binding agent; microaggregates are formed within the macroaggregates; root-derived organic matter plays an important role in aggregate dynamics; the activity of earthworm has a decisive role in micro and macroaggregates formation; SOM is predominantly stabilized in stable microaggregates; and changes in the rate of macroaggregate turnover influence SOM stabilization across soil types and disturbance regimes (Six et al. 2004). The decrease and increase of aggregation stability depend mainly on the soil organic matter (SOM) content. Many researchers reported a strong correlation between SOM content and aggregation stability (e.g. Jakšík et al. 2015; Fan et al. 2020). However, aggregate stability is based on contents of fine sand, silt and clay particles, polyvalent metals (Fe, Al, Ca), and organic matter complexes, which could restrict the accessibility of microorganisms into them (Six et al. 2004).

Organic mulches have been known as a material useful in soil structure stability and soil organic carbon improvement (Kader et al. 2017; Pavlů et al. 2021). The most common organic mulches used to improve crop production are straw, bark or wood chips, leaves, hyacinth, and grass (Amare & Desta 2021). Organic mulches play crucial roles in soil chemical, biological and physical properties, which subsequently affect soil aggregation and soil structure stability (Adekiya et al. 2017). With chemical properties, mulches help to enhance more organic matter and raise the plant nutrients content in the soil, especially in the uppermost soil layer (Qu et al. 2019; Jamir & Dutta 2020). Jamil et al. (2005) also reviewed that mulched soil contributes to more nutrient N, P, K uptake than unmulched soil. Considering biological properties, mulches can diversify the soil microorganisms by providing shelter and food (Yang et al. 2003). Mulched soil contains higher nitrogen amount, which microorganisms require for their metabolism during breaking down organic matter (Sharma et al. 2010; Zhang et al. 2020). With regards to physical properties, mulches could maintain the soil structure, soil temperature, and moisture content by preventing water from evaporation (Ranjan et al. 2017; Kader et al. 2019). The effects of mulches on soil aggregate stability are different according to particular mulch characteristics and mulches quantity (Alharbi 2015; Qu et al. 2019).

This work is a follow-up to the previous research (Pavlů et al. 2021). Within it, the effect of mulches on chemical and hydraulic soil properties was evaluated. Eight different mulch materials (bark chips, wood chips, wheat straw, cardboard, paper foil, decomposable matting, nonwoven fabric covered by bark chips, and crushed basalt) and a control without any mulch were studied during the 4-year period. The most significant effect of mulching was found in the case of the organic carbon content and aggregate stability under organic mulches (straw, bark chips, and wood chips). These materials differ in their chemical composition. All of them contain holocellulose with variable portion of cellulose and hemicellulose, lignin, proteins, and ash. The literature mentions relatively wide ranges of contents of these substances. The straw contains 28–40% cellulose, 21–26% hemicelluloses, 12–25% lignin, and low amount of ash and proteins (Saleem Khan & Mubeen 2012; Lu et al. 2014; Plazonić et al. 2016). The chemical components of bark chips are mainly of holocellulose (37–64% respectively 25–33% hemi-

cellulose), lignin (18–49%), and ash (8–15%) (Mota et al. 2017; Ferreira et al. 2018; Hamad et al. 2019). However, the chemical composition of wood chips is: hemicellulose (34–38%), cellulose (32–35%), lignin (24–37%), and ash (1–4%) (Abdul Khalil et al. 2010; Chen et al. 2010; Waliszewska et al. 2019). A significant difference in the stability of aggregates (index of water stable aggregates (WSA) measured using the procedure of Nimmo and Perkins (2002)) was confirmed (Pavlů et al. 2021). Specifically, aggregates from plots mulched with bark and wood chips were the most stable (WSA – 0.92, respectively 0.91), aggregates from plots under straw were also stable (WSA – 0.84), on the contrary aggregates from the control plots were the least stable of all studied variants (WSA – 0.67). The increase in carbon content was well correlated with the increase in aggregate stability.

The aim of this work is to try to reveal the cause of the higher stability of soil aggregates under organic mulches. A detailed study of separated aggregates and their qualitative properties, among others with the help of infrared spectroscopy (diffuse reflectance infrared spectroscopy with Fourier transformation – DRIFT), can bring new knowledge about stabilization processes, about the role of individual components of organic matter or some mineral soil components.

MATERIAL AND METHODS

Site description. The study site was carried out at the university experimental field in Troja, Prague, Czech Republic. The locality is situated along the Vltava River at an altitude of 196 m. The average annual precipitation is 470 mm, and an annual average temperature is 11 °C. The soil is characterized as Haplic Fluvisol (IUSS Working Group WRB 2014) with sandy loam texture. The experimental design and soil sampling descriptions were described in detail by Pavlů et al. (2021). Twenty-seven plots (each with an area of 4.5 m²) were prepared. Mulches were applied to 24 plots, eight mulch types (bark chips, wood chips, wheat straw, cardboard, paper foil, decomposable matting, nonwoven fabric covered by bark chips, and crushed basalt) in three replications and 3 plots remained as control without mulch. The plots were planted with six perennials, always in the same area scheme (*Geranium sanguineum*, *Hemerocallis*, *Salvia nemorosa*, *Echinacea purpurea*, *Coreopsis verticilata*, and *Heuchera sanguinea*) and without adding of any fertilizers.

Soil sampling. For basic soil characteristic measurements, grab soil samples from 4 punctures per each plot were collected from the surface layer (0–10 cm) using a gouge auger. Samples for aggregate extraction were carefully collected separately using a plastic shovel. Soil sampling was carried out after perennials cutting in October 2018 (last year of experiment). Only the samples from plots mulched with straw, bark, and wood chips were selected and used for this study, because of the significant effect of these mulches on WSA index (Pavlů et al. 2021). Samples from the same year and from control plots were selected and used for a comparison.

Grab soil samples were prepared by the standard procedure for fine earth preparation including drying at 40 °C in the oven, crushing, and then sieving. through the 2-mm sieve. They are referred to soil in the following text. Samples for aggregate extraction were air-dried and aggregates of diameter 2–5 mm were extracted by sieving. The size of the aggregates was chosen in accordance with WSA measuring procedure (Nimmo & Perkins 2002). These aggregates were then crushed for chemical analysis.

Soil analysis. The same chemical parameters were measured for soil and for aggregates. The organic carbon content (C_{ox}) was determined using the rapid dichromate oxidation technique (Sparks 1996).

The humus quality (E4/E6) was analysed according to the spectrophotometric method. The soil samples were extracted using sodium pyrophosphate (0.05 M $Na_4P_2O_7$) and measured by the absorbance ratio at 400 and 600 nm (Sparks 1996, Agilent 8453 UV-Visible spectrophotometer, Santa Clara, USA).

DRIFT spectra were recorded by the infrared spectrometer (Nicolet iS10, Waltham, USA). The spectra with a range of 2.5 to 25 μm (4 000 to 400/cm) were used. The gold mirror was used as a background reference. The 64 scans with resolution 4/cm and Kubelka-Munk units were applied. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., Waltham, USA) was applied for spectra analysis. The potential wettability index (PWI) and index of aromaticity (iAR) were determined using DRIFT spectra (Figure 1). The bands of the alky C-H groups – A (2 948–2 920/cm and 2 864–2 849/cm) were assumed to indicate the hydrophobicity and bands of the C=O groups – B (1 710 and 1 640–1 600/cm) indicate hydrophilicity. The ratio of hydrophobicity and hydrophilicity was used to determine the potential wettability index (Ellerbrock et al. 2005).

$$PWI = A/B \qquad (1)$$

The aromaticity index was calculated according to reflectance of aliphatic bands ranging from
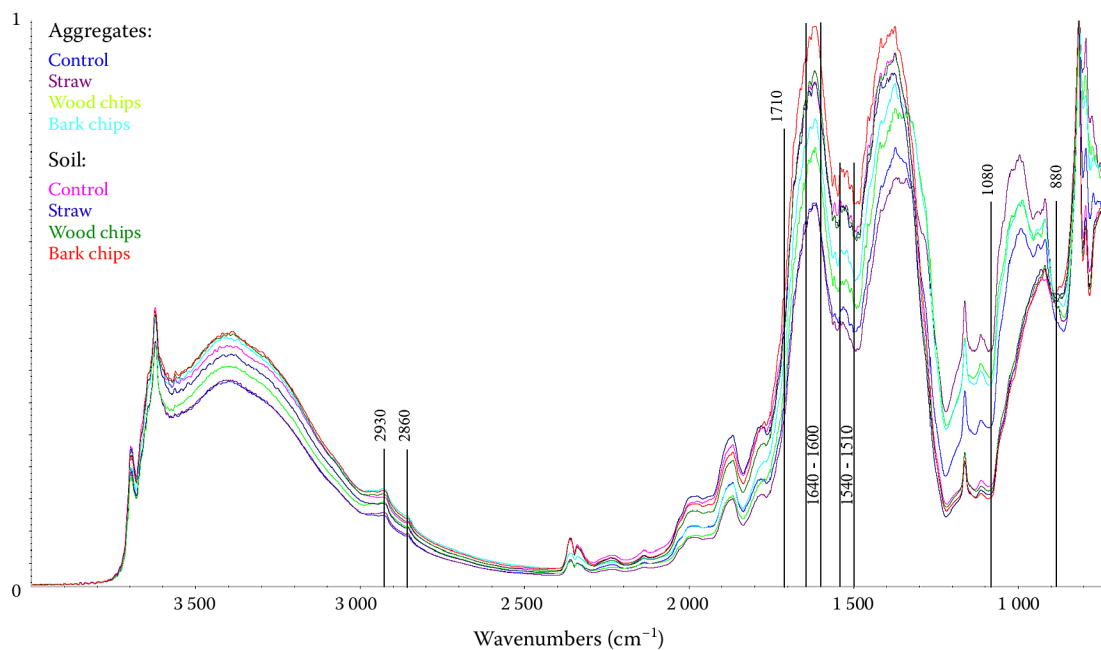

Figure 1. Average diffuse reflectance infrared spectroscopy with Fourier transformation (DRIFT) spectra of studied treatments normalized to the maximum intensity (800/cm)
Position of bands mentioned in paper and used for potential wettability index (PWI) and index of aromaticity (iAR) were marked

3 000–2 800/cm (AL) and aromatic band at 1 520/cm (AR) (Cunha et al. 2009).

$$iAR = AL/(AL + AR) \tag{2}$$

Data analysis. The data were analysed using the software IBM SPSS (Ver. 26). ANOVA was used to define the differences of the primary soil characteristics, potential wettability index, and aromaticity index among the various mulch types (straw, wood chips, and bark chips) and control treatment. *T*-test was used to determine the differences between the two groups (soil and aggregates). Tukey test was performed to express the statistical differences among the treatments.

RESULTS

Figure 1 shows DRIFT spectra of all studied treatments. Each line represented the average of three replications. The spectra were normalized to the maximum intensity that belongs to the quartz band around 800/cm. There were visible differences between soil spectra and powdered aggregate spectra in the wavenumbers range 1 080–880/cm. This part of spectra appertains to bands of secondary silicates located mainly in the clay fraction of soil. Based on the normalized spectra, we can conclude the aggregates contain a higher amount of clays compared to the soil. However, confirmation of this finding by direct texture measurement was not possible due to the small amount of separated aggregates.

The effects of various mulches on soil properties. Table 1 shows that the soils under the wood and bark chips had a higher organic carbon content than the soil under straw and soil on the control plot. Regarding the distribution of humus quality (E4/E6) in the soil, there were no significant differ-

ences among the mulch types ($P > 0.05$). The effects of mulches on the potential wettability index were statistically different in various mulch types. Soils from bark and wood chips treatments had higher PWI compared to the straw and control treatment. The index of aromaticity showed a remarkable difference at $P < 0.05$. Soils from wood chips treatment had the highest iAR, followed by bark chips, straw, and control treatments. If we evaluate soils from mulched plots together and compare their properties with the control plot, a difference can be seen only in the organic carbon content.

Table 2 shows that the content of C_{ox} in aggregates was higher under bark chips and wood chips, than under straw and on control plots. The influence of all studied mulches on humus quality and PWI in aggregates was not found. The iAR of aggregates was significantly different among the various mulch treatments. Aggregates from wood chips, bark chips, and straw treatments had a higher iAR than the control treatment. If we evaluate aggregates from mulched plots together and compare their properties with the control plot, a difference could be seen not only in the C_{ox} content, but also in both evaluated indexes.

The comparison of soil and aggregates. Figure 2 shows the differences between soil and aggregates. There was no significant difference in C_{ox} content between soil and aggregates on control, straw, and wood chips treatment, while the bark chips and a combination of all mulches types showed a statistical difference between soil and aggregates (A). Regarding the humus quality (E4/E6), there were no obvious differences in all treatments (control, straw, wood chips, bark chips, and combination of all mulches) (B). The effects of mulches on the PWI of aggregates were observed in straw, bark chips, and a combination of all mulch

Table 1. The various effects of different mulch types on soil properties

Mulches	C_{ox}	*CV*	E4/E6	*CV*	PWI	*CV*	iAR	*CV*
Control	*1.52 ± 0.102*[b]	6.68	3.67 ± 0.303[a]	7.36	0.024 ± 0.002[b]	2.08	0.045 ± 0.005[b]	8.89
Straw	*1.64 ± 0.199*[b]	12.10	3.87 ± 0.106[a]	3.44	0.023 ± 0.002[b]	14.35	0.043 ± 0.004[b]	6.98
Wood chips	*2.33 ± 0.280*[a]	12.03	3.73 ± 0.400[a]	10.35	0.029 ± 0.002[a]	15.86	0.054 ± 0.006[a]	9.26
Bark chips	*2.47 ± 0.092*[a]	3.71	3.77 ± 0.066[a]	4.83	0.027 ± 0.003[a]	20.00	0.050 ± 0.006[ab]	10.00
All mulches	2.14 ± 0.42*	19.63	3.78 ± 0.21	5.56	0.026 ±0.003	11.54	0.049 ± 0.006	12.24

C_{ox} – soil organic carbon (in %); E4/E6 – humus quality; PWI – potential wettability index; iAR – index of aromaticity; average values ± standard deviations, *CV* – coefficient of variation (in %); small letters indicate the significant differences among the mulches types at $P < 0.05$; *significant difference between control and mulched variants computed together; values written in italics were adopted from Pavlů et al. (2021)

Table 2. The different effects of various mulches on soil properties in aggregates

Mulches	C_{ox}	*CV*	E4/E6	*CV*	PWI	*CV*	iAR	*CV*
Control	1.45 ± 0.254^b	14.22	3.75 ± 0.219^a	6.30	0.025 ± 0.006^a	8.00	0.048 ± 0.000^b	2.08
Straw	1.9 ± 0.156^b	6.86	3.70 ± 0.794^a	19.33	0.033 ± 0.006^a	4.85	0.063 ± 0.006^{ab}	11.11
Wood chips	2.69 ± 0.211^a	6.35	3.92 ± 0.052^a	5.26	0.035 ± 0.006^a	5.14	0.074 ± 0.025^a	24.32
Bark chips	3.07 ± 0.435^a	11.65	4.01 ± 0.525^a	10.83	0.035 ± 0.006^a	6.86	0.065 ± 0.015^{ab}	15.39
All mulches	$2.55 \pm 0.57^*$	22.35	3.87 ± 0.45	11.63	$0.034 \pm 0.005^*$	14.71	$0.067 \pm 0.014^*$	20.90

C_{ox} – soil organic carbon (in %); E4/E6 – humus quality; PWI – potential wettability index; iAR – index of aromaticity; average values ± standard deviations, *CV* – coefficient of variation (in %); small letters indicate the significant differences among the mulches types at *P* < 0.05; *significant difference between control and mulched variants computed together

types. Higher PWI was found in the aggregates than in the soil. In the wood chips and control treatment no significant difference between soil and aggregates was found (C). The comparison of iAR showed significant differences in straw treatment and in the case of all mulch combination between soil and aggregates. Aggregates were found to have higher iAR than soil.

DISCUSSION

The soil organic carbon (C_{ox}) is more pronounced after mulching. Wood and bark chips showed the highest content of C_{ox} followed by C_{ox} content under straw. The higher C_{ox} content under bark and wood chips was probably due to the quality of organic mat-
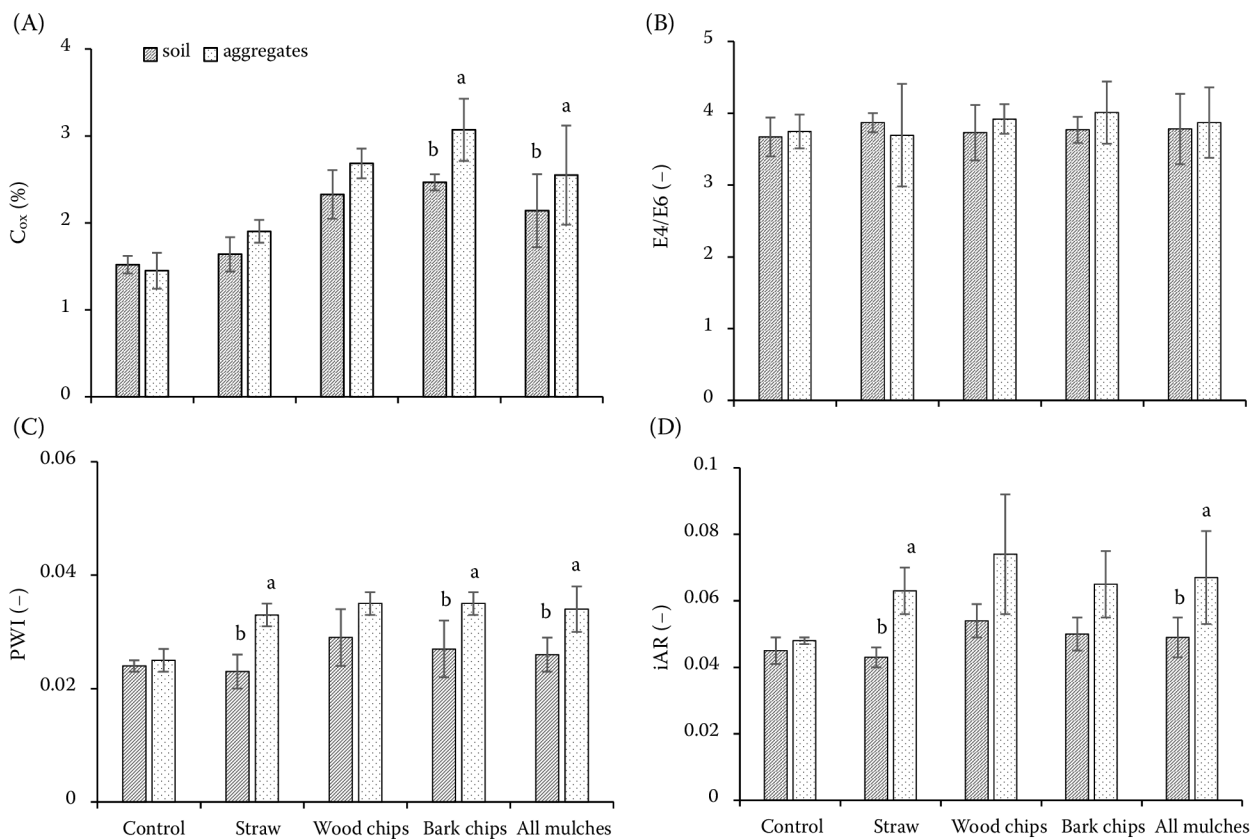
Figure 2. Average values of soil organic carbon (C_{ox}) (A), humus quality (E4/E6) (B), potential wettability index (PWI) (C), and index of aromaticity (D) separately for treatments

All mulches – a combination values of straw, wood and bark chips; the error bars correspond to the ± standard deviation values; columns followed by different letters indicate significant differences between soil and aggregates according to the significant difference *t*-test, *P* ≤ 0.05

ter and a higher content of recalcitrant in bark and wood. It was agreed with the findings of Luna et al. (2016) confirming that the higher concentration of C_{ox} could result from the quality and quantity of organic residues, and probably due to hardly decomposable materials (recalcitrant) as e.g. lignin, litter decaying and root exudate from the plant species in the experimental field. Contrary, a lower C_{ox} content in straw treatment than wood and bark chips ones could be possible due to less lignin content and higher content of easier decomposable cellulose in straw (Tozluoğlu et al. 2015). Straw provided more water-soluble substances (pectin, organic acids, free amino acids, and mineral elements) into the soil solution, which was the source of nutrients and energy for microbial growth and decomposition (Gao et al. 2016). Rapid decomposition of organic materials caused the C_{ox} loss through CO_2 volatilization, C leaching, and plant uptake (Turmel et al. 2015). In addition, a comparison between the soil and aggregates showed that the concentration of C_{ox} was higher in aggregates than in the soil (Figure 2). This could indicate that aggregates were stabilized and improved due to the binding agents through organic materials adsorbed, together with an electronic binding between negative charges of clay minerals and positive charges of oxides, and a coat of oxides on the surface of mineral forms bridged from one particle to the others (Six et al. 2004; Tivet et al. 2013). Nonetheless, once aggregates were stabilized, they could protect the C_{ox} from leaching, dissolving, reducing the accessibility for microbial decomposition, and for interacting between pores insides and outside of the aggregates (Goebel et al. 2005; Leue et al. 2015; Zhao et al. 2021).

In our result, the PWI was more pronounced after applying organic mulches to the soil surface. The wood and bark chips treatments had a higher soil PWI compared to straw and control. It is probably due to the less mineralization rate and because the wood and bark chips themselves contain more recalcitrance compounds and reduce microbial decomposition (Goebel et al. 2005). A comparison between the soil and aggregates (Figure 2) showed that straw, bark chips, and a generally organic mulching are able to enhance PWI in aggregates. The secondary metabolites produced from decomposing organic matter can be extremely hydrophobic, particularly from fungal exudates and hyphae (Hallett & Young 1999). Higher PWI values point to lower aggregate wettability, which caused a decrease in infiltration rates (Haas et al. 2018). However, the lower wettability

could also result from the accumulation of organic compounds (terpenes and waxes), which came from the root and earthworm activity (Haas et al. 2018). Six et al. (2004) reviewed that high SOM content could lower wettability due to the increasing hydrophobic characteristics of SOM and the formations of various additional intermolecular associations during drying. Many researchers documented that once SOM content and compositions were improved, it could enhance the capacity of absorbing and retaining more moisture in the aggregates (Bajoriene et al. 2013; Hosseini Bai et al. 2014; Leue et al. 2015). Besides that, the clay-organic surface of aggregates is also able to decrease the potential wettability (Leue et al. 2010), which was supported by our result from the infrared spectroscopy showing the high content of clay fractions in the aggregates. Fér et al. (2016) found that the wettability of surface aggregates could be reduced by various mineralogical compositions of the clay (i.e., illite) in coating and interiors. It was also documented by Ellerbrock et al. (2009) that the rate of water and solute mass transfer could be decreased because of the influences of clayey aggregate coatings and lining along the biopores in the surface.

The variation of aromaticity index was significantly higher in the wood, bark chips, and straw treatment than in the control treatment. A comparison between soil and aggregates revealed that the straw and all mulch types showed higher iAR in aggregates than in the soil. This could indicate that mulches, especially straw, enhanced more aliphatic compounds in the aggregates. The greater iAR could result from the increase of SOM mineralization, which contained the aggregated-related aliphatic compounds (Jakab et al. 2019) and could be related to the proportion of aromatic compounds (lignin, phenols, and alkyl-aromatics) in the materials (Laudicina et al. 2015; Wiedemeier et al. 2015). Corvasce et al. (2006) reported that the aromatic compounds exist differently according to the plant residues and could be released into the soil through microbial decomposition. The aromatic compounds are likely to adsorb onto the soil particles rather than dissolve (Corvasce et al. 2006). Moreover, soil disturbance like tillage or soil stirring is expected to increase aromaticity in the aggregates-occluded soil organic matter (Jakab et al. 2019).

CONCLUSION

After applying the organic mulches (straw, wood chips, and bark chips), the content of C_{ox} was found

higher in the aggregates than in the soil. On the other hand, the infrared spectroscopy showed the aggregate spectra of all variants including control without mulch had higher reflectances of the secondary alumosilicates than in the soil spectra. This indicated that these minerals abundant in clay fraction play an important role in aggregate creation, but differences in aggregate stability are mainly affected by organic compounds. Higher values of the aromaticity index mean a relatively lower proportion of aromatic components, or a higher proportion of aliphatic components of organic matter in stable aggregates than in unstable aggregates from the control plot. These substances are also considered to be hydrophobic and are therefore able to protect the aggregate from dispersion with water, which is confirmed by the higher values of the potential wettability index for stable aggregates from mulched plots.

Another more general result of the article is that infrared spectroscopy can provide useful information about the qualitative parameters of soils, both mineral and organic. In contrast, the E4/E6 ratio, commonly used to evaluate the quality of organic matter, proved to be less sensitive in this case.

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7.3. Temporal changes in soil chemical compositions in acidified mountain forest soils of Czech Republic

Thai, S., Pavlů, L., Tejnecký, V., Chovancová, S., Hin, L., Thet, B., Drábek, O. (2023). Temporal changes in soil chemical compositions in acidified mountain forest soils of Czech Republic. European Journal of Forest Research. 142, 883–897. https://doi.org/10.1007/s10342-023-01564-x

Temporal changes in soil chemical compositions in acidified mountain forest soils of Czech Republic

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Abstract

The study aimed to investigate the temporal changes of pH, sorption complex, and structure of soil organic matter through the forest soil profile under beech and spruce forests located in Jizera mountains (Czech Republic) and affected by natural and anthropogenic acidification. Soil samples were collected in four different years (2008, 2013, 2015, and 2020) in each horizon: fermented horizons (F), humified horizons (H), organo-mineral horizons (A), and subsurface mineral horizons (B) (cambic or spodic). The cation exchange capacity (CEC), base saturation (BS), exchangeable element contents, pH, and soil organic carbon content (SOC) were determined. The infrared soil spectra were used to calculate indices of potential wettability, aromaticity, and decomposition. Our results showed that most nutrients and aliphatic compounds were retained in the uppermost soil layers. The aromaticity of organic matter increased with depth, while polysaccharides, regarding the decomposition compound, disappeared through the soil horizons. In a long-term observation, SOC content had constantly increased under beech, while spruce remained stable in the organic horizons. Exchangeable element contents increased in each horizon, except for Al and Fe; their content quickly decreased in F horizons and slowly decreased in H horizon under both forest tree species, while the deeper horizons remained constant, but increased in A horizon under spruce. Continuously increasing base cations concentrations in sorption complex of both forest tree species during the study period revealed the effect of forest stand types on acid deposition reduction and mitigation. The temporal changes in CEC, BS, SOC, and soil wettability are more intensive in beech than in spruce forest floor.

Keywords Soil properties · Infrared spectroscopy · Forest ecosystem · Environmental acidification

Introduction

Globally, climate change, soil degradation, and carbon loading in the atmosphere have been concerned and have drawn attention from environmental research and policy agendas (FAO 2017). Forest disturbances including natural and anthropogenic disturbances (e.g., drought, deforestation, agriculture, and forest fire) are one of the most important in responding to global climate change (Sommerfeld et al. 2018). Acid depositions are also included to affect the forests negatively. In the mid-nineteenth century, industrialization and coal mining were rapidly increased with poor regulation and lacked abatement technology; as a result, the nitrogen and sulfur contained in coal ranging from 1 to 15% had been combusted and emitted (Oulehle et al. 2007; Achilles et al. 2021) and caused a large area of European forests and soils severely disturbed and damaged (Krug and Frink 1983; de Vries et al. 2014). Acid deposition adversely affects the soil chemistry and forest ecosystem by increasing the proton H^+ concentration, leaching of base cations, and mobilization of Al and other potential toxic elements into the soil (Likens et al. 1996; Johnson et al. 2018; Pavlů et al. 2021). Moreover, acid deposition has been reported as a driver dismissing the diversity in the terrestrial ecosystem (Duprè et al. 2010). Oulehle et al. (2007), who studied the long-term effect of

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tree species on soil acidification in the Ore Mountains, found that depletion of base cations resulted in a low base saturation of 8% under spruce and 6.5% under beech forest. On the other hand, some other studies about the long-term recovery from acidification found that the forest soil has been improved in cation exchange capacity, base cations, and total carbon and declined Al concentration in the organic horizons. However, in some severely affected sites, the soils were slowly recovered and did not suddenly return to a good environmental condition, as previously seen (Hruška et al. 2002; Oulehle et al. 2017; Hédl et al. 2011; Johnson et al. 2018). Therefore, changes in disturbance dynamics and forest management need to be implemented and observed in order to sustain ecosystem diversity and mitigate climate change.

Beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L.) are the most abundant forest tree species in Central Europe and have been studied for their various influences on long-term changes in soil physical, biological, chemical properties after acidification (Berger and Berger 2012; Pavlů et al. 2018; Tejnecký et al. 2013). Generally, forest tree species differ in the soil properties such as pH, exchangeable cations, nutrient cycle, soil fertility, and SOC stabilization due to their quality and quantity of litter, root exudation, nutrients uptake, and litter decomposition, depositional processes (interception of deposition such as throughfall, bulk deposition, and stemflow) canopy uptake and leaching (Bradová et al. 2015; Habumugisha et al. 2018). For instance, forest litter such as leaves, branches, and roots from beech and spruce varies in its composition, quality, and quantity. It provides different nutrients with different availability for plants, and decomposition rate through soil microorganisms (Han et al. 2021). Many researchers pointed out that the spruce litters are decomposed more slowly than litters found in the beech forest because they contain a high amount of recalcitrant substances (i.e., lignin, resin, waxes, and phenolic compounds) (Nacke et al. 2016; Richardson and Friedland 2016). Slower decomposition leads to slow cycling of nutrients but stabilizes SOC in the soil profile (Cremer and Prietzel 2017). The SOC stabilization takes place according to the abiotic and biotic processes (Campbell and Paustian 2015) and goes through these mechanisms: conservation due to recalcitrance, the interchange of elements, and inaccessibility to the decomposer community due to the occlusion in the aggregate soil (Poirier et al. 2018). The content of nutrients such as nitrogen (N), calcium (Ca), potassium (K), and phosphorus (P) in the coniferous forest soils is also likely lower than in deciduous forest soils (Iwashima et al. 2012) due to less decomposition and mineralization. It is also shown by Berger et al. (2006) that beech had higher Ca content than spruce due to the association with the effect of Ca-pump under beech resulting from transpiration of beech and uptake water from deeper soil horizons, in which the soil solution contains more Ca because of weathering supply of the bedrock. Oulehle and Hruška (2005) studied the effects of specific tree species (beech and spruce) in the long-term acidified forest and found that beech forest had a higher accumulation of Ca and K in the soil than spruce forest, but lower concentration of Al. Spruce is considered a strong acidifier and can deplete the base cations in the topsoil layer, whereas beech performs as the Ca-accumulator and increases Ca in organic horizons (Daněk et al. 2019). The high concentration of Ca in the soil relatively increased soil pH, nutrients, base saturation (BS), and biodiversity (Iwashima et al. 2012).

The study hypothesized that beech and spruce forests are able to recover effectively from anthropogenically enhanced acidification and promote soil organic matter and soil nutrients in the forest ecosystem in the long term. The study mainly focused on: (1) evaluating the temporal changes of sorption complex, exchangeable elements and structure of SOM through the forest soil profile and (2) differentiating the chemical soil structures of SOM between beech and spruce forest affected by acidification. However, the infrared spectroscopy was used to evaluate the chemical soil structures of SOM, which were indicated by some indices.

Materials and methods

Site description and soil sampling

The study was carried out in the Jizera Mountains, in the northern part of the Czech Republic along the border with Poland. The region was heavily affected by acid deposition and is one of the most damaged areas in Czech Republic during the 1980–1990 period because of the nearby coal-fired power plant (black triangle – Czech-German–Polish border) (Moldan and Schnoor 1992; Suchara and Sucharová 2002; Sucharova et al. 2011). Mean annual deposition rates in recent years ranged between 2.6 and 8 g NO_3^-/m^2 and between 2.6 and 20 g SO_4^{2-}/m^2, while before 1990 the deposition of these acidifiers reached levels higher than 5 g of sulfur and 3 g of nitrogen /m^2 (CHMI 2023a, b). However, Kopáček and Veselý (2005) reported that S deposition declined linearly from 1990 to 2000, while N deposition declined rapidly during 1989–1994 and then slowly afterward. The composition of the forest tree species in Jizera Mountains in between 2012 and 2020 ranged from 7.7 to 14.9% in beech forest and from 48.8 to 69.1% in spruce forest (Podrázský et al. 2014; Zemědělstvi 2021). The sampling locality is called Paličník (50.8683900N, 15.2527000E), where it has been monitored for a long time (Borůvka et al. 2009; Bradová et al. 2015; Tejnecký et al. 2010, 2013); therefore, it was selected for this research as a long-term observation. The elevation of the sampling locality ranges

from 635 to 680 m a.s.l. The average annual precipitation is between 600 and 1200 mm, and the average temperature is roughly between 5 and 9 °C (Remrova and Císlerová 2010; Balcar et al. 2012). However, there was a dry climatic condition in 2015 during the study period observed by Ionita et al. (2017) and shown in Fig. 1. The main vegetation is dominated by the European beech (*Fagus sylvatica* (L.)) within the natural ecosystem of the occurrence of perennial grasses in ground vegetation (*Calamagrostis arundinacea, Calamagrostis villosa*), and spruce monoculture forest (Norway spruce: (*Picea abies* (L.) Karst.) along with perennial grasses (*Calamagrostis arundinacea, Calamagrostis villosa*). The average height of the forest stands is about 32.4 m in beech forest and 28.6 m in the spruce forest (Bradová et al. 2015). Additionally, the soils were characterized as Aluminic Cambisol under beech forest and Entic and Haplic Podzol under spruce (Tejnecký et al. 2010, 2013, 2014). Soil bedrock was determined as medium-grained porphyritic biotite granite to granodiorite (Cháb et al. 2007). The thickness of the soil layers is very variable under both forest tree species due to slope and the randomly selected soil pits for sampling in each year (supplementary information, table S1).

The samples were taken in different years (2008, $n = 24$; 2013, $n = 24$; 2015, $n = 56$; and 2020, $n = 24$). Three individual soil pits (50×50 cm) were dug at each species sites (spruce and beech) in 2008, 2013, and 2020, but seven soil pits were dug in 2015. The soil samples were taken in different soil horizons: fermented horizons (F), humified horizons (H), organo-mineral horizons (A), and subsurface mineral horizon (B) (cambic horizon under beech, spodic humususesquioxidic horizon and cambic horizon enriched with iron oxides under spruce). The soil pits were randomly selected, and the distance of the pits was at least 15 m. The soil samples were air-dried and sieved to 2 mm particles. The soil samples for measurements with infrared spectroscopy were milled to fine fractions using Fritsch Analysette 3 Spartan Pulvensette miller, Idar-Oberstein, Germany.

Soil characteristics analysis

The active pH (pH_{H2O}) was determined in a ratio of 1:4 (soil:water, w:v) for organic horizons and 1:2 for mineral horizons. The suspension was shaken for 5 min and then measured using the pH-electrode SenTix 21 (Inolab pH level 21, WTW, Germany). The SOC content was determined by rapid dichromate oxidation ($K_2Cr_2O_7$) techniques following Tyurin´s method (Sparks 1996). The total cation exchange capacity (CEC) was determined according to the standard ICP Forest methods (Cools and De Vos 2016). The exchangeable cations were measured in 0.1 M $BaCl_2$ (2.5:30 w/v ratio) extract of the soil using AAS (SpectrAA Varian 280FS, Australia) and ICP-OES (iCAP 7000, Thermo Scientific, USA). Exchangeable acidity (EA) was calculated from the sum of Al^{3+}, Fe^{3+}, Mn^{2+}, and H^+, and base cation (BC) was calculated from the sum of Ca^{2+}, Mg^{2+}, Na^+, and K^+. The cation exchange capacity was calculated by summing up all cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+}, Fe^{3+}, Mn^{2+}, and H^+). The quality control and quality assurance of all laboratory procedures were done according to standard protocol.

Diffuse reflectance infrared Fourier transform spectroscopy

The milled soil samples were measured using an infrared spectrometer (Nicolet iS10) and OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., USA). Due to the darkness of forest soil samples, the spectra were recorded by 120 scans in wavenumbers ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The measured reflectance was converted to Kubelka–Munk units (KM), and the gold mirror was used as the background of the spectra (Thai et al. 2021).

Fig. 1 The average temperature (°C) and precipitation (mm) under beech and spruce from 2008 to 2020 in the locality— Hejnice meteorological station (CHMI 2023a, b)
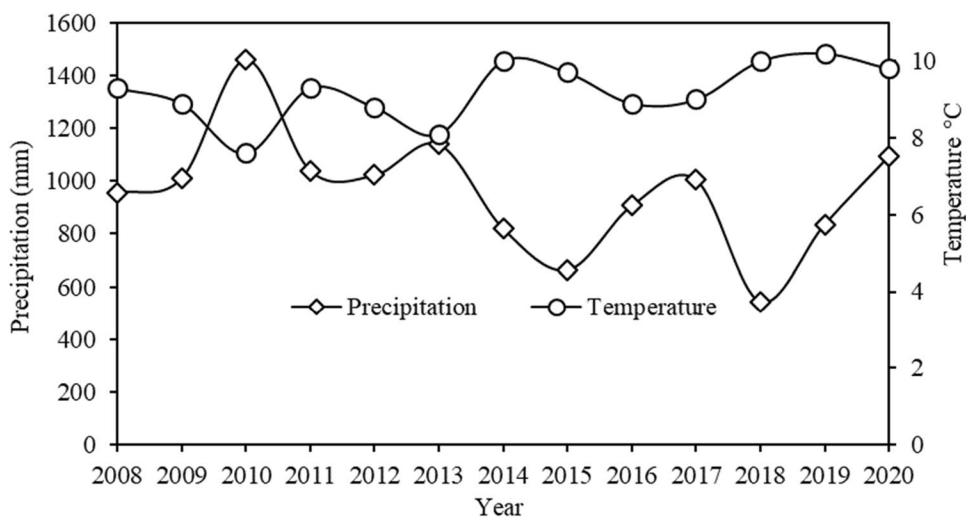
The potential wettability index (PWI), aromaticity index (iAR), and decomposition index (iDEC) were determined using DRIFT spectra. The adsorption bands ranging from 2948 to 2920 cm^{-1} ascribed the asymmetric C–H stretch vibrations, and the adsorption bands ranging from 2864 to 2849 cm^{-1} attributed to the symmetric stretch vibrations. The adsorption band at 1710 cm^{-1} ascribed C=O groups in ketones, carboxylic acids, and amides. The adsorption bands ranging from 1640 to 1600 cm^{-1} referred to carboxylate and aromatic groups (Gerzabek et al. 2006), and OH bending vibrations of water molecules in hydration layers of soil phyllosilicates (Leue et al. 2010). The potential wettability index (PWI) was evaluated according to the adsorption band of the alky C–H groups – A (2948–2920 cm^{-1}), indicating the relative hydrophobicity, and adsorption band of the C=O groups—B (1740–1698 and 1640–1600 cm^{-1}), which is ascribed to hydrophilicity. PWI was calculated as a ratio by summing up the intensity of the C–H and C=O groups (PWI = A/B) (Ellerbrock et al. 2005). The higher index value indicated the lower wettability of the soil (Haas et al. 2018). Index of aromaticity (iAR) was calculated from the absorption band of aliphatic bands intensity – AL (3000–2800 cm^{-1}) and aromatic bands intensity – AR (1520 cm^{-1}), (iAR = AL/(AL + AR) (Cunha et al. 2009). The higher mean values of iAR expressed a lower proportion of aromatic compounds in the soil. The index of decomposition (iDEC) was based on the absorption band of carboxylate and aromatic groups – X (1640–1600 cm^{-1}) and polysaccharides—Y (1030 cm^{-1}). The iDEC was calculated by summing up the intensities of the C=O group and polysaccharide intensity and then performed as a ratio (iDEC = X/Y) (Artz et al. 2006). The high value of iDEC indicated finer particles and more decomposed organic matter because of the loss of intensity of polysaccharides (Preston et al. 1987; Haberhauser et al. 1998).

Data analysis

The temporal changes of pH, sorption complex, exchangeable elements and structure of SOM during the study period and through the soil horizons were statistically assessed using analysis of variance (ANOVA) at error level of 0.05 (confidence level of 95%). T test was used to differentiate the chemical compositions between the forest tree species (beech and spruce). The statistical differences among the soil horizons (F, H, A, B) and between forest types were presented in alphabetical letters using the Tukey test. To run the data correctly, the homogeneity of variances was applied to check its normality. These statistical analyses were evaluated using software IBM SPSS (version 26, New York, USA). Besides that, a correlation matrix and principal component analysis (PCA) were also performed to access co-variations and evaluate the relationships among the chemical compositions using the R studio program (Jollife and Cadima 2016; Girona-García et al. 2018).

Results and discussion

Soil pH

The forest soils were found to be more acidic in the organic horizons than in the subsurface mineral horizons (F, H, A, < B) under both forest tree species. The result showed same pattern as the study by Borůvka et al. (2009). However, more acidic nature in the organic horizons and with time in Fig. 2 resulted from litter decomposition and acid deposition (Hedl et al. 2011; Yang et al. 2015). The SOM decomposition was considered to lower soil pH due to the interaction and exchange with Al (Cremer and Prietzel 2017) and increased amount of H$^+$ resulted in more acidic soil in the uppermost layer (Zaidey et al. 2010). As a comparison between the forest tree species, the soil pH found no significant difference, but the pH value in spruce soil was found to be lower than under beech forest soil in all years and horizons (Fig. 2) which is in accordance with findings of Daněk et al. (2019).

The cation exchange capacity and exchangeable elements

The cation exchange capacity statistically decreased with depth (F > H > A > B) in all years under beech and spruce (Fig. 2). The decrease in CEC revealed that less cations were retained in lower horizons than in the uppermost soil layers and relatively corresponded with high organic material inputs and SOC content during litterfall. Soil organic carbon, generally, plays a vital role in CEC in cation binding and soil sorption complex in the organic and mineral horizons (Ciarkowska and Miechówka 2019; Cremer and Prietzel 2017). Our results (Fig. 5) confirmed that CEC was strongly correlated ($r = 0.83$, $P < 0.001$) with SOC, indicating that CEC increased with increased SOC concentration. Besides that, during the plant uptake, it brings more nutrients to accumulate in the uppermost horizons because of the high proportion of nutrients absorbed in the roots and recycled nutrients through litterfall, stemflow, and throughfall (James et al. 2016; Johnson et al. 2018; Langenbruch et al. 2012; Oulehle et al. 2007).

Regarding the time changes, the CEC increased significantly from 21.6 ± 3.5 to 33.7 ± 3.6 cmol + kg^{-1} in F horizon, 13.9 ± 2.8 to 15.2 ± 0.8 cmol + kg^{-1} in H horizon, 7.6 ± 2.8 to 11.3 ± 0.8 cmol + kg^{-1} in A horizon, and 4.1 ± 1.9 to 7.2 ± 1.1 cmol + kg^{-1} in B horizon under beech. Remarkably, the CEC in 2015 was observed to have the lowest values in F and H horizons under beech. It was similar to the CEC in
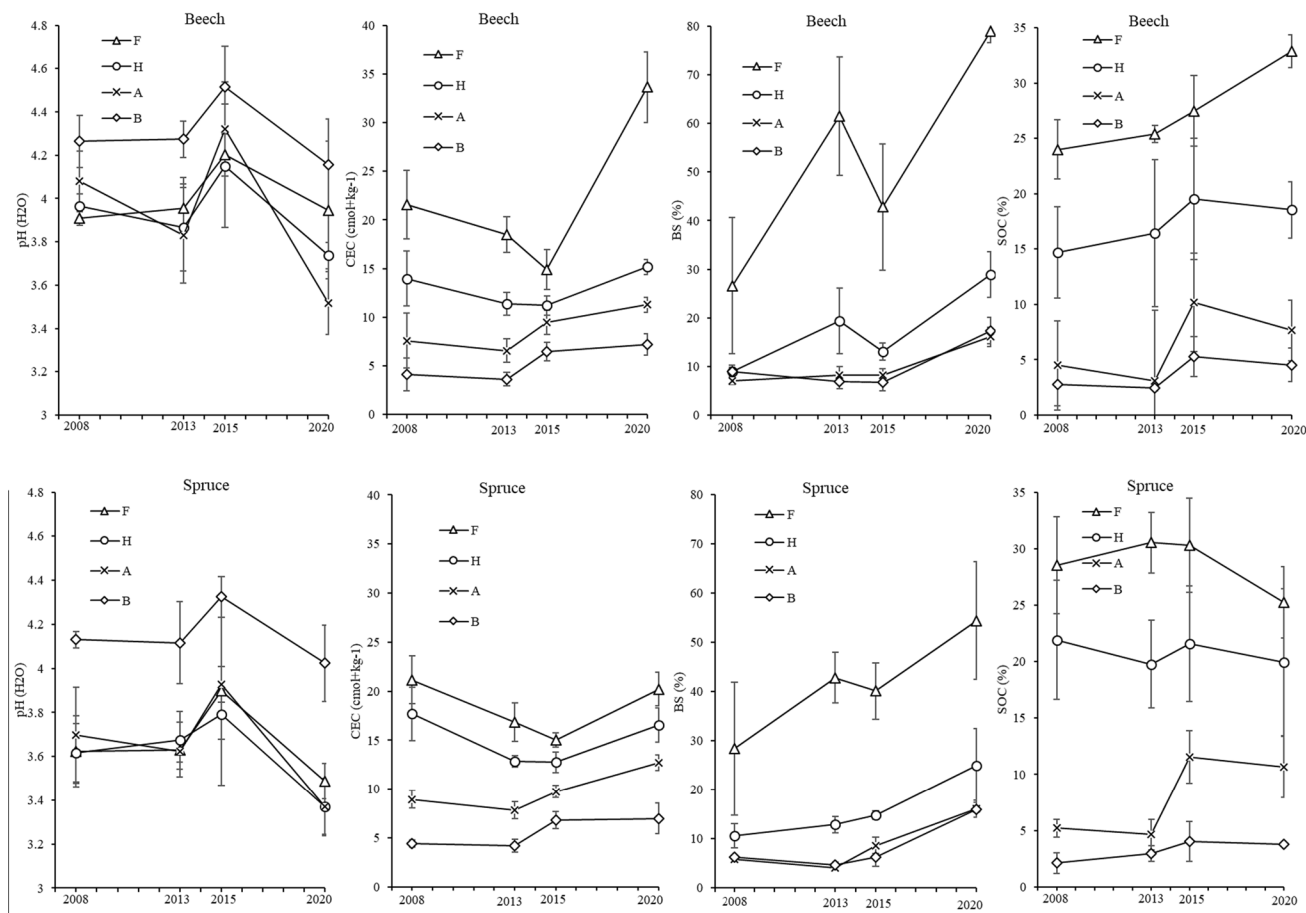
Fig. 2 The distribution and temporal changes of soil chemical characteristics in fermented horizon (F), humified horizon (H), organomineral horizon (A), and subsurface mineral horizon (B – spodic or cambic) of the soil profile dug under beech and spruce at Jizera Mountains (Czech Republic). (Mean and standard deviation; 2008, $n = 24$; 2013, $n = 24$; 2015, $n = 56$; and 2020, $n = 24$). Base saturation (BS—%), cation exchange capacity (CEC—cmol + kg^{-1}), soil organic carbon (SOC—%)

spruce forest, which showed no specific pattern in F and H. The CEC decreased from 2008 to 2015 but recovered slowly in 2020, while A and B showed increasing CEC with time (Fig. 2). The lowest CEC in 2015 in F and H horizons in beech forest was associated also with the decrease of BS. However, the dry climatic conditions (high temperature and low precipitation) in 2015, which is observed in Fig. 1 and by Ionita et al. (2017), decreased nutrients and their recycling due to less adsorption with the organic matter and the decrease decomposition of forest litter (Mondal 2021; Gelybó et al. 2018). For comparison between forest tree species, significant differences in the CEC were observed ($P = 0.004$) in F horizon in 2020 (beech > spruce). This result was consistent with the same finding of Mareschal et al. (2010). Tree species compositions affected the soil in various ways (Cremer and Prietzel 2017). Beech forest was considered to have large foliage nutrients and lower foliage lignin content than spruce forest that accelerated litter decomposition and bioturbation and enhance organic layers

with high base cations (Berger and Berger 2012). This corresponds to our results from soil spectra as indices (Fig. 4) and our results in supplementary information (Table S2) that show nutrients under beech such as Ca^{2+} and Mg^{2+} increased significantly from 2008 to 2020 in all horizons, while spruce was relatively constant (no significance) in F and H horizons (Table S2). However, it indicated that spruce used the nutrient stock efficiently, while beech was more likely to hold, cycle, and stock nutrients in the forest floor (Bublinec and Machava 2015; Bagherzadeh et al. 2008). It was in agreement with the research of Matschonat and Falkengren-Grerup (2000), who found Ca^{2+} and Mg^{2+} increased tendency in beech forest after recovering from acid deposition. High acidity and poor decomposition of litters under spruce in the locality contributed to higher Al^{3+} concentration and more mobilization in the forest, leading to depleting the base cations and indicating a slow recovery of nutrients in sorption complex in spruce forest (Oulehle and Hruška 2005; Collignon et al. 2011; Daněk et al. 2019).

Notably, it was observed that the number of exchangeable elements decreased significantly with depths in all years except for Al^{3+} (Table S2). Aluminum content decreased significantly with depths (F, H > A, B) in 2008. This suggested that, in 2008, Al concentration remained more mobilized in the organic horizons due to the atmospheric acid deposition that occurred during 1980–1990. On the contrary, in 2013, 2015, and 2020, Al^{3+} concentration was observed to be accumulated more in H and A horizons under both forest tree species, which resulted from increases in organic acids from the decomposition in the soil and the initial stage of weathering of minerals in mineral phases (Akbar et al. 2010; Iwashima et al. 2012). On the other hand, Dijkstra and Fitzhugh (2003) reported that it may have originated from Al release after SOM decomposition and also from the increased Al dissolution induced by low soil pH. Regarding the long-term study in beech, the Ca^{2+}, Mg^{2+}, K^+, Na^+, and Mn^{2+} were statistically changed by their increasing concentrations (2020 > 2015, 2013, and 2008), while Fe^{3+} decreased in F horizon with a range from 1.2 ± 0.3 to 0.25 ± 0.09 cmol + kg^{-1} but increased in H and A horizon ranging from 0.8 ± 0.3 to 1.1 ± 0.1 cmol + kg^{-1} and 0.4 ± 0.1 to 1.0 ± 0.3 cmol + kg^{-1}. Despite that, Al^{3+} concentration quickly decreased from 12.4 ± 1.9 to 1.6 ± 0.5 cmol + kg^{-1} in F horizon and slowly decreased from 11.1 ± 2.0 to 7.6 ± 1.3 cmol + kg^{-1} in H horizon, while A and B horizons remained stable (no significance) under beech. There was similar tendency in spruce, the concentration of Al^{3+} significantly decreased from 9.8 ± 2.8 to 3.9 ± 1.7 cmol + kg^{-1} in F horizon and from 11.3 ± 0.9 to 8.3 ± 1.3 cmol + kg^{-1} in H horizons but increased in A horizon ranging from 6.5 ± 0.7 to 7.2 ± 0.3 cmol + kg^{-1}. This suggested that a larger part of Al^{3+} was bound in the organic complexes that had been leached from the soil or might be sorbed on soil mineral phases (Borůvka et al. 2009). The higher amount of SOM in the organic horizons (Fig. 2) also indicated that the soil sorption sites were mainly by organic matter that suppressed Al toxicity by decreasing dissolved Al^{3+} activities in surface soils (Berthrong et al. 2009; Borůvka et al. 2009; Dijkstra and Fitzhugh 2003). The mechanism of SOM contributes to the variations of Al^{3+} and Fe^{3+} by exchanging the polyvalent cation-bridging between negative charges of organic matter (Mueller et al. 2012). Likewise, the low concentration of Al^{3+} and Fe^{3+} in F horizon and decreases with time in organic horizons resulted from the direct interaction with atmospheric conditions (temperature and precipitation) (Bradová et al. 2015) and also revealed the effects of forest tree species in long-term soil acidification, less acidic deposition from the atmosphere in the study area, and the podsolization process in spruce forest (Altman et al. 2017; Krug and Frink 1983; James et al. 2016). An increase of Al^{3+} in A horizons with time under spruce resulted from the high acidity in the organic soil solution due to the aluminosilicate weathering (Oulehle and Hruška 2005). Additionally, continuously increasing nutrients in both forest tree species during the study period revealed the effect of forest tree species on acidity deposition reduction and mitigation.

Soil organic carbon, indices of soil wettability, aromaticity, and decomposition

In both beech and spruce forests, the content of SOC decreased through soil horizons (F > H > A > B) in each year. Generally, the effect of forest on SOC led to more accumulation in the topsoil layers (F and H) compared to deeper soil profiles. This resulted from the living and dead plant matter accumulating in the uppermost layers (Habumugisha et al. 2018; Langenbruch et al. 2012; Galka et al. 2014).

After a decade of observation, beech and spruce had no significant changes in SOC in the F, H, and B horizons, but A horizons showed a significant increase from 4.5 ± 4.0 to $7.7 \pm 2.8\%$ in beech and from 5.2 ± 0.1 to $10.7 \pm 2.7\%$ in spruce. Remarkably, beech forest showed SOC content increased constantly in average values with time ranging from 24.0 ± 2.7 to $32.0 \pm 1.5\%$ in F horizon, from 14.7 ± 4.1 to $18.0 \pm 2.6\%$ in H horizon, and from 2.8 ± 1.9 to $4.5 \pm 1.5\%$ in B horizon, while spruce remained relatively stable in most horizons (Fig. 2). Besides that, there was a statistical increase of SOC in beech ($P = 0.041$), once all values were combined from soil horizons. It was opposite to spruce, where no significant difference was observed ($P = 0.441$). As a comparison between beech and spruce using a T test, there were significant observed differences ($P = 0.032$) in F horizon in 2020, where beech had markedly higher SOC content than spruce (Fig. 2). A lower concentration of SOC under spruce than in beech was not usually found. Numerous studies confirmed that spruce promoted more organic carbon and higher thickness layer of organic horizons in a long-term observation due to the higher recalcitrant substances (e.g., lignin, resin, waxes, and phenolic compounds), which were difficult to be decomposed by microorganisms (Andivia et al. 2016; Grüneberg et al. 2019). It was in contrast to our findings. This resulted from the local environmental condition and different forest stands such as age, density, and canopy forest (Yuan et al. 2013). Bradová et al. (2015), who studied the same locality, reported that the beech forest was older than spruce, by approximately 80 years, and had larger canopy closure (87%) than spruce (40%). The higher density and age of the forest stands in the research area had typically larger basal area of trees, in which it enhanced SOC in the forest soil (Menyailo et al. 2022). It was consistent with the finding of Yuan et al. (2013) who found that SOC was stored higher under the old-growth forest trees. The larger canopy of the beech forest stands, however, reduced the decomposition rate, while an open canopy led to SOC loss due to more favorable soil microclimates, higher exposure to throughfall

and to the warmer condition, which accelerated the decomposition, leaching, and soil respiration by microorganism (Zech et al. 1989; Merabtene et al. 2021; Hanakova-Becvarova et al. 2022; Jandl et al. 2022). It was also documented by Fang et al. (2005) regarding the variation of SOC level with the temperature and by Andivia et al. (2016) about the relationship between SOC and canopy.

Besides that, the constant increases in average values of SOC content in each horizon in beech forest during the study period revealed the larger forest productivities (litterfall) and more SOC inputs that were expected from the compensation from soil acidification by beech forest. The primary sources of organic carbon are not only from the litterfall but also from soil microorganisms, root exudates, and root litters (Andivia et al. 2016; Li et al. 2015; Nickels and Prescott 2021). Roots system is one of the main factors in the distribution of SOC under forest tree species (Tefs and Gleixner 2012). Beech stands, in fact, had a larger and deeper anchored root system, which provided higher belowground biomass and caused SOC to be more distributed into the soil horizons (Laganière et al. 2010; Hansson et al. 2011). Ohno et al. (2014), who observed the molecular composition and biodegradability of soil organic matter, found that deciduous forests had higher root dead mass and root mortality than coniferous forests, and thus enhanced

higher aliphatic content in the forest soil. Together with the root exudate, it improved long-term soil organic carbon storage by adsorption onto the mineral surface under deciduous forests.

On the other hand, the behavior of SOC and other elements is associated with soil wettability, aromaticity, and decomposition, and vice versa (Artz et al. 2006; Cunha et al. 2009; Ellerbrock et al. 2005; Ellerbrock and Gerke 2013). Therefore, our study extended further information about the relationship among the chemical components using DRIFT spectroscopy. The spectra in Fig. 3 clearly showed the differences in the chemical compositions through soil profile under both forest tree species.

The potential wettability index (PWI) declined statistically through the soil profile (F > H > A > B) from each year under both forest tree species. This means that organic horizons had lower wettability (F and H horizons) than the mineral horizons (A and B horizons). A similar result was found by Woche et al. (2017) and Atanassova et al. (2018). The different PWI through the soil profile indicated the importance of SOM inputs in the soil through their vertical transporting processes (root growth and SOM distribution) (Leue et al. 2010). The high PWI in the organic horizon was confirmed by a high SOC content with high hydrophobicity, which lowered soil wettability and reduced the infiltration rate (Goebel
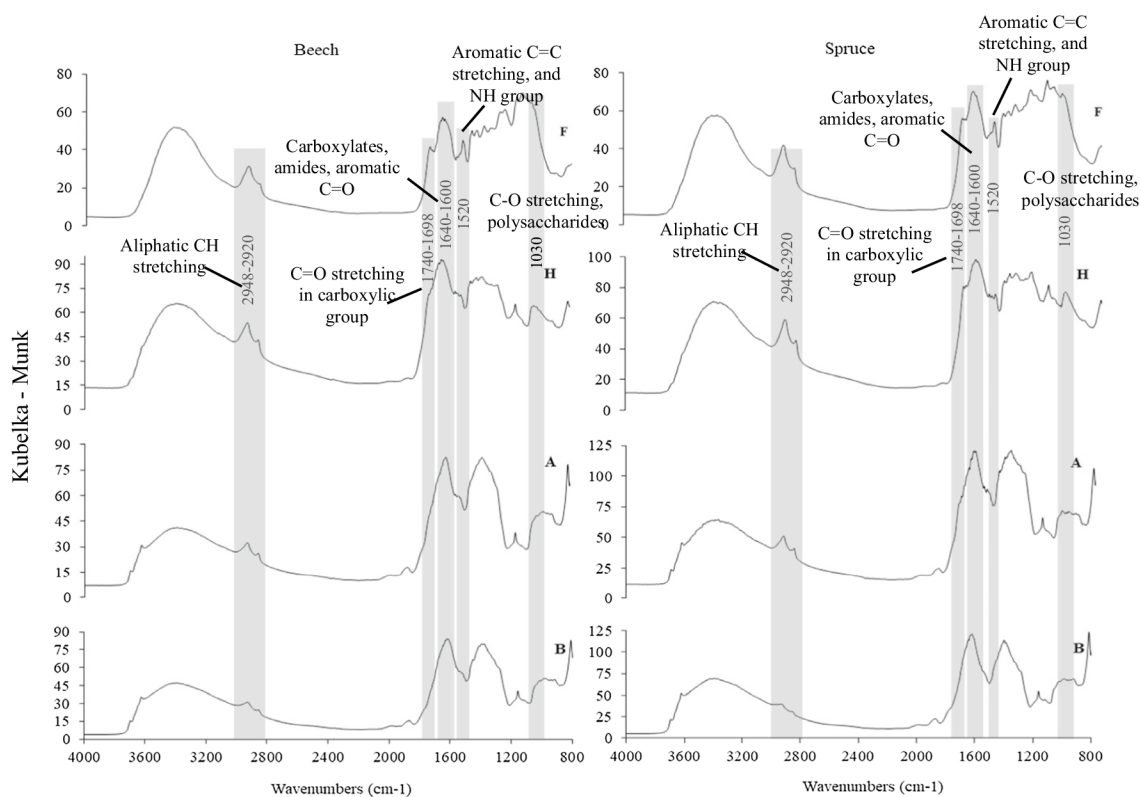

Fig. 3 The representative of average DRIFT spectra of soil in beech and spruce under different soil horizons (Fermented horizons (F), humified horizons (H), organo-mineral horizons (A), subsurface mineral horizons (B—spodic or cambic); $n = 24$) in 2020

et al. 2005). The process of SOC in soil wettability had few mechanisms. The hydrophobicity decreased wettability by reducing the surface free energy of the soil, restricting the soil from wetting (Turski et al. 2022) and decreasing the rehydration rate (Eynard et al. 2004). However, the SOC improved the soil porosity by holding soil particles together against external disturbances (Eynard et al. 2004). The variation of PWI through the soil profile was also associated with the abundant root system, and high Ca content in the organic horizons that enhanced soil rhizosphere and indicates strong incorporation between Ca and OM, which possibly stabilizes aliphatic contents that further increased PWI (Leue et al. 2010; Ohno et al. 2014; Turski et al. 2022). A strong correlation was highlighted between Ca and PWI ($r = 0.58$, $P < 0.001$) in Fig. 5.

Regarding a long-term observation, PWI increased significantly from 0.17 ± 0.02 to 0.24 ± 0.01 in F horizon and 0.13 ± 0.02 to 0.20 ± 0.02 in H horizons under beech, while spruce relatively remained stable (no significance) in all horizons. The increases of PWI with time revealed a lower soil wettability and enhanced SOC and aggregate stability (Woche et al. 2017). It can be said that SOM improved PWI (lowering wettability) and high PWI prevented SOC from microbial decomposition (Atanassova et al. 2018). In a comparison between forest tree species, there were significant differences observed in F and H horizons in 2015, where spruce had a higher index, but in 2020, beech had a higher PWI in F horizon. This was consistent with the increase in SOC content in 2020 (Fig. 2). Beech produced more residues and had deeper root system compared to spruce; therefore, it enhanced organic carbon better and sequestrated faster into the soil profile. With this, it significantly affected the PWI (Eynard et al. 2004; Ilek et al. 2015). On the other hand, it was observed that there was a strong correlation between PWI and SOC ($r = 0.89$, $P < 0.001$) (Fig. 5). Hence, the variation of PWI was explained according to the tendency of SOC. This was also supported by Ellerbrock and Gerke (2013) who explained that the SOM compositions regulated the soil wettability and sorption and transfer properties of the flow pathway.

The aromaticity index decreased dramatically with increasing soil profile depths (F > H > A > B), which means the aromatic content increased with depths. A similar result was found by Zech et al. (1989) and Silva et al. (2022), showing that the content of aromaticity increased from L to B horizons. It was contrast to the finding of Ohno et al. (2014) where the abundance of condensed aromaticity of SOM was much lower in subsoil under coniferous and deciduous forests due to the adsorption of aromatic compounds to the minerals present in the soil profiles. The decrease or increase of the iAR through the soil profile, generally, depends on the association of plant residue compositions, climate conditions, and microorganism present in the soil

(Koutika et al. 2020; Thai et al. 2022). The lower aromaticity in the uppermost soil layer than in the deeper soil profile under both forest tree species, however, was indicated by the less humified and decomposed organic matter due to the chemical and physical interaction mechanisms (Chen et al. 2013; Corvasce et al. 2006). Ussiri and Johnson (2003) found that the decomposition of forest residues relatively affected the aromaticity index changes through the soil horizons. Nonetheless, the aromaticity in the soil profile had been shown to increase with degrees of decomposition and maturity of OM (Chefetz et al. 1998; Margenot et al. 2015; Veum et al. 2014). Aromatic compounds were less susceptible to become mobile; therefore, they are likely retained in the mineral soil horizon (Bi et al. 2013). Zech et al. (1989) reported that the aromatic compounds in the spodic soil profile were increased due to the leaching of phenolic substances during the podsolization.

After a decade of observation, the iAR changed significantly by increasing from 0.29 ± 0.04 to 0.36 ± 0.01 in F horizon under beech, while spruce had no statistical changes in all horizons. To compare between the two forest tree species, there were significant differences observed in F, H, and A horizons in 2015, where spruce had a higher index than beech, but in the F horizon in 2020, beech had a higher iAR. The changes of iAR by increasing with time in F horizon under beech indicated the degree of SOM decomposition and more aliphatic compounds that dominated in this soil horizon (Pizzeghello et al. 2017). It is also shown in Fig. 5 that iAR was correlated with SOC ($r = 0.89$, $P < 0.001$) regarding iAR increase with increasing SOC content. The remaining constant iAR under spruce and in subsoil was due to the preferential retention of condensed and substituted aromatic molecules, which are recalcitrant to mineralization processes (Corvasce et al. 2006; Gangloff et al. 2014). Furthermore, aromatic compounds were more likely adsorbed onto the soil particles than mobile in the soil solution through the soil profile (Thai et al. 2022; Ohno et al. 2017). Besides that, the high inputs of root lignin and cool climate in the study sites were considered as a cause of stability in the aromaticity content in the soil under spruce and in the subsoil horizons (Zech et al. 1989; Silva et al. 2022).

The index of decomposition displayed no significant difference through the soil horizons in 2008 and 2013 in beech and spruce in 2008 ($P > 0.05$). Contrary to 2015 and 2020, the iDEC significantly changed by increasing with depth under both forest tree species. Similar results were shown by Prasad et al. (2000) that the iDEC increased with depth. The increases of the iDEC through the soil profile indicated that the intensities peak of polysaccharides (1030 cm^{-1}), which indicated one of the primary energy sources contained in the plant residues, were dramatically declined from F to B horizons by various moieties of forest litter substances (Haberhauer et al. 2000). This result was agreed with Nuzzo

et al. (2020) who found that that the intensity of polysaccharides spectral band decreased with depth. On the other hand, the carboxylic and aromatic compounds, which were relatively linked with the lignin structures, were less vulnerable and resistant to microbial attack, while polysaccharides were decomposed easily by microorganisms in the organic horizons (F and H horizons) (Tseng et al. 1996; Artz et al. 2006). Additionally, Fig. 5 shows that there was a negative correlation ($r = -0.63$, $P < 0.001$) between iDEC and iAR. In long-term observation during the study period, the iDEC significantly increased from 1.3 ± 0.3 to 1.9 ± 0.2 in B horizon under beech and from 1.4 ± 0.1 to 1.7 ± 0.2 in A horizon under spruce. This resulted from a high amount of inorganic substances in A and B horizons that caused the changes in the intensity peaks of organic matter, which affected the decomposition index (Prasad et al. 2000; Haberhauer et al. 1998). In comparison between the forest stands, there were no significant differences between forest tree species in most of the soil horizons in each year except for F and H horizon

in 2008 and B horizon in 2015, which showed a significant difference ($P = 0.05$, 0.014, and 0.018, respectively) between forest tree species (beech > spruce). The higher iDEC found in beech than spruce revealed that beech had more decomposable materials than spruce and provided more variable nutrients in the forest soil.

Correlation matrix and principal components analysis (PCA) among the soil properties

Figures 4 and 5 show the correlation matrix and PCA results among the soil properties. The length of the vectors indicated the strength of their contribution to each PC. Vectors pointing to similar directions were positively correlated; vector directions contrary to each other were negatively correlated; directions of vectors at 90° angle were not correlated. The PCA was grouped by year with four different colors for each year. Markers on the same side described a high contribution on the variable dataset with 95% confidence ellipse
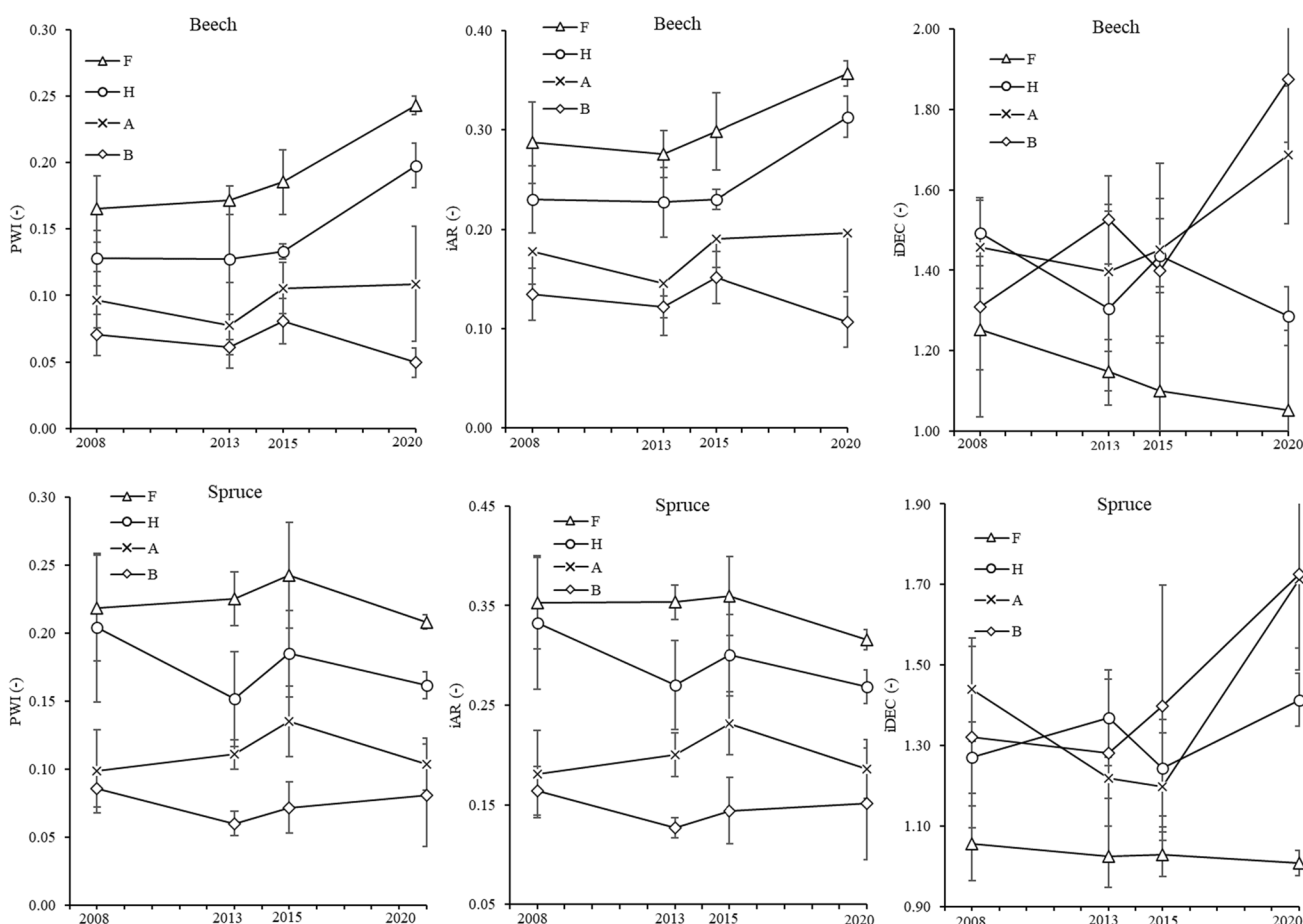

Fig. 4 The distribution and temporal change of the potential wettability index (PWI), index of aromaticity (iAR), and index of decomposition (iDEC) in fermented horizons (F), humified horizons (H), organo-mineral horizons (A), subsurface mineral horizons (B—spodic or cambic) of the soil profile dug under beech and spruce at Jizera Mountains (Czech Republic). (Mean and standard deviation; 2008, $n = 24$; 2013, $n = 24$; 2015, $n = 56$; and 2020, $n = 24$)
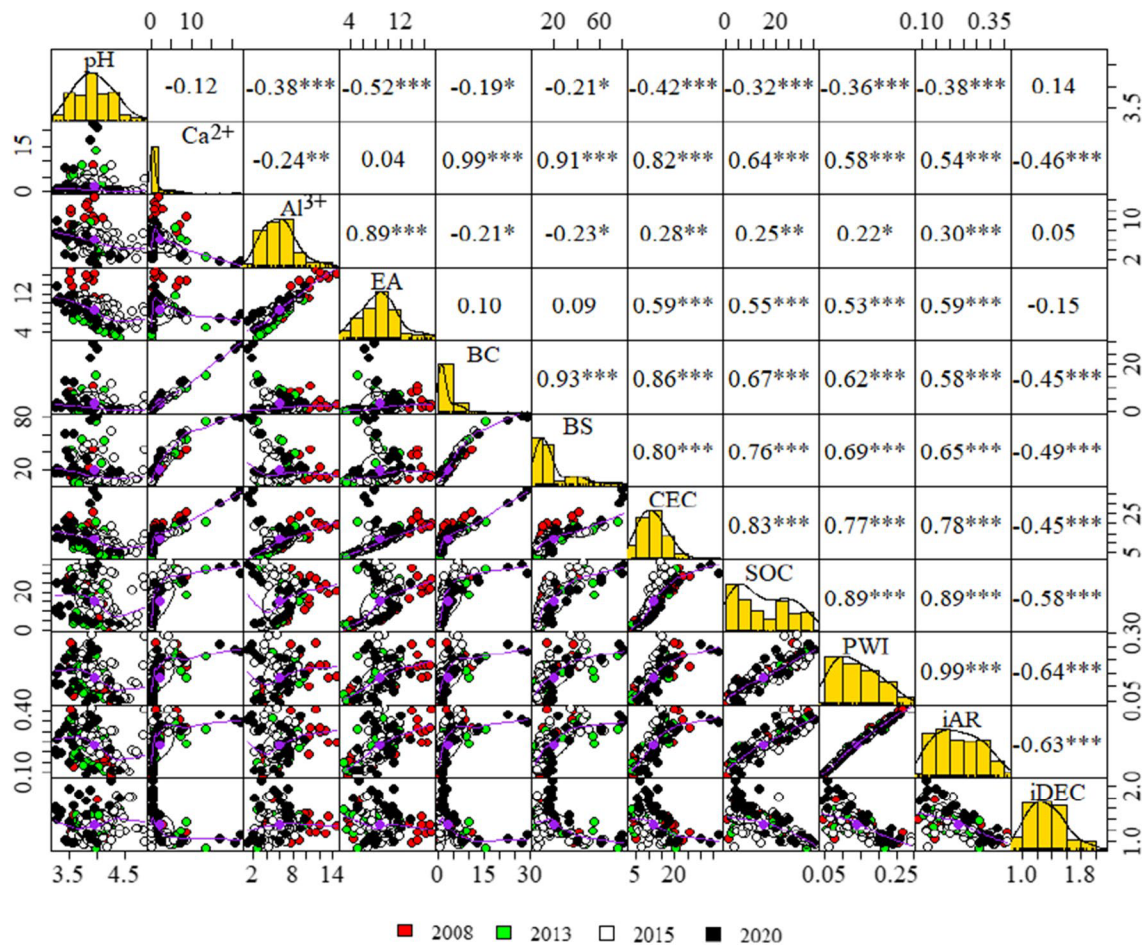
Fig. 5 Correlation matrix plot of all data among the soil properties under forest tree species. (Note: *, **, *** correlation significant at 0.05, 0.01, and 0.001, respectively). (2008, *n* = 24; 2013, *n* = 24; 2015, *n* = 56; and 2020, *n* = 24). Ions concentration in sorption complex—(Ca^{2+}, Al^{3+}, exchangeable acidity—EA, and base cation—BC (cmol + kg^{-1})), base saturation (BS (%)), cation exchange capacity (CEC (cmol + kg^{-1})), soil organic carbon content (SOC (%)), potential wettability index (PWI (-)), index of aromaticity (iAR (-)), and index of decomposition (iDEC (-))

(Escobar-Flores et al. 2019). There were eleven principal components with eigenvalue > 1. The principal component analysis, which selected the main soil properties, showed the first two PCs as 79.8%. The first axis of PC1 was 57.8%, and the second axis of PC2 was 22.0% of the total variance (Fig. 6). Most of the soil properties such as SOC, PWI, iAR, CEC, BS, BC, and Ca^{2+} positively contributed to PC1 and PC2, whereas the $pH_{(H2O)}$ and iDEC were negatively associated. The correlation matrix, however, showed that PWI, SOC, BS, CEC, iDEC, and iAR were closely correlated with each other. A similar correlation among these properties was described by Ellerbrock and Gerke (2013) and Solly et al. (2020) and further discussion was in our results mentioned above. Surprisingly, the ellipse of the year 2008 (Fig. 6) showed the same direction of EA and Al^{3+} and then gradually moved their directions toward Ca^{2+}, BC, BS, CEC, SOC, PWI, and iAR in 2013, 2015, and 2020. This indicated that soil in 2008 maintained high concentration

and mobilization of Al^{3+} and Fe^{3+} and was also proved the influences of the forest tree species on the recovery and mitigation of the soil properties from acidification in a long-term observation.

Conclusion

The study agreed with the hypothesis that beech and spruce forests are able to recover effectively from anthropogenically enhanced acidification and promote soil organic matter and soil nutrients in the forest ecosystem in the long term after massive decline of atmospheric acids deposit during the 1990s. The cation exchange capacity and soil organic carbon content under both forest tree species were higher in the organic horizons than the mineral horizons. After a decade of observation, it was proven that some soil horizons, especially in F and H horizons, were

Fig. 6 Principal component analysis (PCA) biplot combining the main observed variables that contributed to the distribution and temporal changes of soil properties in all horizons of the forest soil. (2008, $n = 24$; 2013, $n = 24$; 2015, $n = 56$; and 2020, $n = 24$)
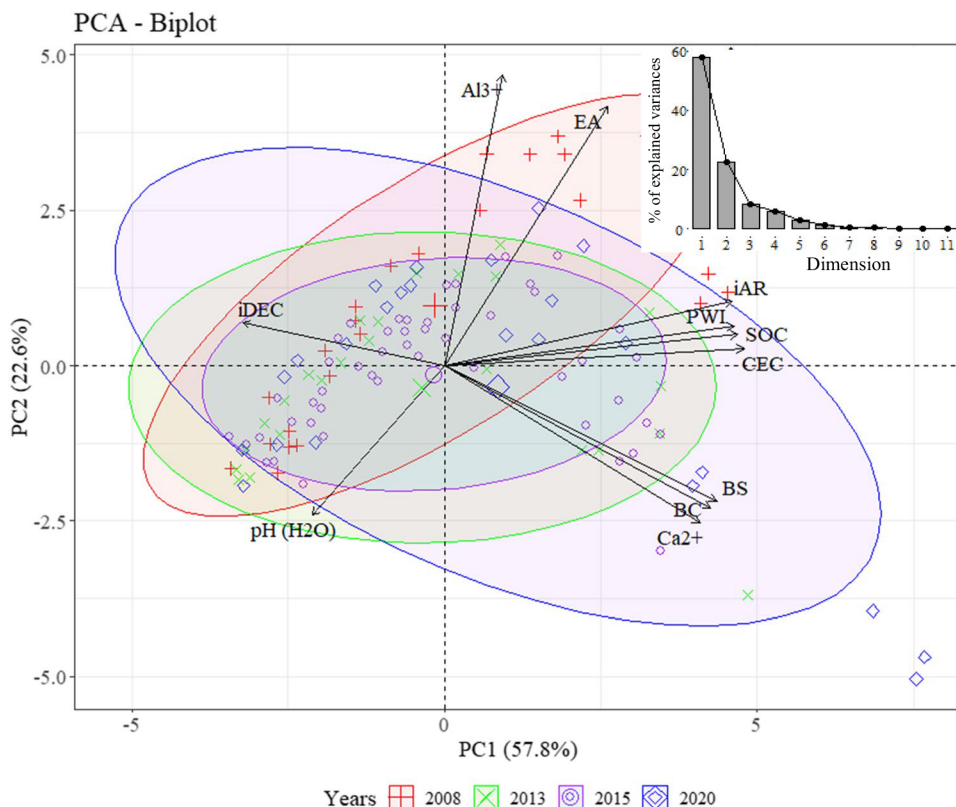
more pronounced in changing the soil chemical properties under both forest stand types. The exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) which were depleted from acidification have been significantly increased with time under both forest stands. Moreover, it was observed that the nutrients were more variable under beech forest in all horizons than in spruce stands due to more decomposable materials, larger canopy and productivity of litter, and less acidity in the soil. However, the drought in 2015 was considered to lower the exchangeable elements in the organic horizons (F and H horizons). Additionally, Al and Fe content quickly decreased in F horizons and slowly decreased in H horizon under both forest tree species. This indicated that Al and Fe were bound in the organic complexes that had been leached from the soil or might be sorbed on soil in mineral horizons. It was also observed that SOC content increased constantly in values under beech, while spruce remained stable. Nonetheless, the soil wettability decreased in F and H and aromaticity index increased in F horizon with time under beech, which signified that SOC improved and aliphatic group proportion increased in organic horizons. As a result, we assumed that beech forest was better in reducing and mitigating of the soil acidification than spruce one. Moreover, beech stand improved soil to more favorable conditions for future plant growth.

Declarations

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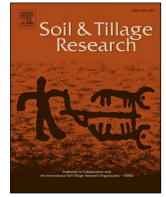
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7.4. **Prediction of the distribution of soil properties in deep Colluvisols in different pedogeographic regions (Czech Republic) using diffuse reflectance infrared spectroscopy.**

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Prediction of the distribution of soil properties in deep Colluvisols in different pedogeographic regions (Czech Republic) using diffuse reflectance infrared spectroscopy

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ABSTRACT

Colluvisols form a significant part of the erosion–deposition soil catena mainly in undulating, agriculturally managed landscapes. Due to their sedimentary origin, they are soils with highly variable properties. For such diverse and often extremely deep soils, it is essential to capture the vertical distribution of properties in as much detail as possible. This study demonstrates the potential of the diffuse reflectance infrared spectroscopy (DRIFT) to derive accurate information on the stratigraphy and selected soil properties (soil organic carbon and calcium carbonate contents and aluminium and iron concentrations) of deep colluvial profiles in three regions in the Czech Republic with different dominant soil types (Chernozem, Luvisol, and Cambisol). The normalization of the spectrum using the quartz spectral band was found to be suitable for assessing the carbonate content in Chernozems and Luvisols (coefficients of determination (R^2) were 0.89 and 0.88, respectively). The amount of organic carbon can be predicted from such normalized spectra with less confidence ($R^2 = 0.64$). Organic matter quality as an indicator of their stability and maturity was computed from aliphatic compounds spectral bands (2930 cm^{-1}) and aromatics and C$=$O groups band around 1640 cm^{-1}. The highest values of this indicator were found in Colluvisols in the Chernozem region (> 6, while, e.g., in the Cambisol region it is < 1), especially in the layers corresponding to the oldest sediments or buried in-situ horizons. In the Cambisol region, the buried B horizon was identified based on normalized (i) clays and Fe oxides bands and (ii) wider band of OH groups, which in this case is related to the content of iron oxyhydroxides. The study proved that the applied set of spectral parameters is an effective tool for the description of diverse soil parameters and for identification of the boundaries of individual soil layers. It is equally suitable for carbonate-free soils as well as for soils with higher carbonate contents, which usually cause difficulties in the interpretation of soil organic matter spectral parameters. It provides a comprehensive view of the soil and its mineral and organic components and can provide information that is difficult to measure by other methods.

1. Introduction

Colluvisols are a specific soil type arising at the foot of slopes or side valleys due to the sedimentation of eroded material transported from the wider area. They are a record of climatic fluctuations, changes in land use and varying soil tillage (Leopold and Völkel, 2007). Colluvisol formation varies between the sedimentation of relatively thick layers during intensive rainfall episodes and the slow accumulation of thin layers in drier periods (Zádorová and Penížek, 2018). The most

commonly considered factors affecting the erosion intensity and formation of colluvial soils include: (i) transformation of forested areas and grasslands to agricultural land, enhancing soil redistribution through both the acceleration of surface runoff due to the removal of the stable vegetation cover and the disturbance of the soil balance, in particular the deterioration of the soil structure, leading to a higher susceptibility of the soil to erosion removal (Boardman and Poesen, 2006), (ii) landscape defragmentation, leading to the establishment of large homogeneous agricultural blocks and, conversely, the disappearance of natural

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or artificial features acting as a barrier to translocated soil material, slowing down the surface runoff and retaining the surplus of water and material on the field (Foucher et al., 2014), (iii) intensive agriculture with use of heavy machinery and deeper, often up- and downslope, ploughing (Van Oost et al., 2006), causing displacement of material, i.e. tillage erosion, disturbance of soil aggregates and soil compaction, increasing the susceptibility to material removal during rainfall episodes, and (iv) crop rotation with long periods of bare soils, often leaving the land without vegetation cover during critical spring periods with increased occurrence of heavy rainfall events (Keesstra et al. (2016)). Decreasing tillage depth and ploughing along the contour lines, management of plant residues, intercrops and winter crops or grass margins are considered as feasible methods to reduce the intensity of soil material redistribution due to soil erosion (Van Oost et al., 2006; Kincl et al., 2022). The Czech landscape has undergone extreme changes in the last 70 years, related to the politically motivated collectivisation of agricultural production and the massive consolidation of agricultural land (Sklenička et al., 2014). The disappearance of landscape elements, the use of heavy machinery and the increase in the field size, together with undulating relief and vulnerable soils, led to intensive material redistribution not only in the most exposed loess areas (Sarapatka et al. (2018)), but also in the hilly regions with magmatic or metamorphic bedrock dominating in the Czech Republic (Zádorová et al., 2023). Colluvisols can reach considerable thicknesses and act as soil organic carbon reservoirs (Chaopricha and Marín-Spiotta, 2014; Zádorová et al., 2015). They can help to understand the causes and consequences of actual and past soil erosion, and they attract more attention as a key to our understanding of the landscape dynamics in the changing climatic conditions (Dotterweich, 2008).

To date, Colluvisols have been studied by a complex of different methods and approaches, revealing different aspects of their formation and post-depositional pedogenesis, first predominantly in loess regions (e.g., Zádorová et al., 2013; Kühn et al., 2017; Kołodyńska-Gawrysiak et al., 2018; Sherer et al., 2021a), more recently also in areas built on a wide range of non-loessic parent materials (Henkner et al., 2018; Kappler et al., 2018; Kaiser et al., 2020; Scherer et al., 2021b; Zádorová et al., 2023). Attention is paid mainly to the assessment of the age of individual layers. Optically stimulated luminescence (OSL), often in combination with the radiocarbon method, has been widely used for the datation (e.g., Fuchs and Lang, 2009; Poręba et al., 2015). Determination of radionuclide activity (^{137}Cs, ^{210}Pb, ^{10}Be, $^{239+240}$Pu) and human-bound vertically stable substances, such as organic pollutants (e. g., DDX, HCB), potentially risk elements or nutrients, can also be effectively used to assess both recent and long-term deposition (e.g., Clemens and Stahr, 1994; Zádorová et al., 2013; Poręba et al., 2019; Loba et al., 2022). The potential of their use is related to their affinity to soil components, mainly soil organic matter and clay, and thus a relatively low vertical mobility in the soil profile (van der Perk, 2006). Since for many substances the period of beginning or cessations of their use or input into the soil is known, it is possible to relate the increased concentrations of substances in a particular layer to a specific period of deposition (Zádorová et al., 2023). At the same time, the sedimentary soils provide an important record of the intensity of use of these compounds, including an understanding of the leaching process and residence time in the profile, which are essential for taking practical measures in soil management. The study of a wide range of chemical and physical parameters (Zádorová et al., 2013; Jakšík et al., 2015; Scherer et al., 2021a; Pavlů et al., 2022), soil micromorphology (e.g., Kühn et al., 2017), mineralogy (e.g., Dreibrodt et al., 2013, Zádorová et al., 2023) and microbial properties (e.g., Sagová-Marečková et al., 2016) can elucidate and describe a variety of depositional and pedogenetic processes alternating during the formation of these soils. However, most of these analyses are quite demanding in terms of time and instrumentation.

There are also less laborious indirect techniques using various types of sensors to identify elements or minerals in the soil profile, and organic matter content. Often used are portable X-ray fluorescence spectrometry and visible and near-infrared spectroscopy (Stockmann et al., 2016; Benedet et al., 2022; Gozukara et al., 2022) in studies focusing on soil profile differentiation.

Infrared (IR) spectroscopy in the middle infrared part of spectra (wavelength 2.5–25 μm; 4000–400 cm^{-1} respectively) is frequently used for the identification of pure chemicals. Part of the spectral range referred to as fingerprint (1500–400 cm^{-1}) is specific for different functional groups vibration in molecules. It depicts relatively sharp and well-identified peaks of specific spectral bands (Stuart, 2004). A more complicated situation is with spectra of mixtures where bands of individual functional groups overlap. Soil is a typical mixture containing a wide range of mineral and organic components. Thus, wider bands appear in the spectra (Haberhauer et al., 1998; Madejová, 2003; Leue et al., 2010; Le Guillou et al., 2015; Tinti et al., 2015) and the identification of individual substances is thus considerably limited. For example, OH group vibration in the range 3440–3320 cm^{-1} can belong to organic matter components or to minerals of group oxide–hydroxides. Spectral peak around 1520 cm^{-1} can belong to the C=C vibration of benzene rings together with the amid II functional group. Cunha et al. (2009) use this band for the calculation of index describing the aromatic components proportion in organic matter, while Haberhauer et al. (1998) uses it as an indicator of the decomposition of organic matter depending on the content of its nitrogenous components. Moreover, in the case of soil formed on carbonates substrates, this peak is entirely covered by a broad and intensive carbonates band. One of the approaches to analyse IR spectra is the evaluation of spectra as a whole and obtaining information with advanced mathematical operations (e.g., Ng et al., 2019). Partial least squares regression is the most common chemometric method used in the prediction of soil properties from diffuse infrared reflectance spectra (Minasny and McBratney, 2008). Other alternatives for spectral data processing and modelling can be using robust artificial intelligence approaches to solve problems exhibiting complex mechanisms, particularly in geoenvironmental engineering (Jalal et al., 2021) if a large data set is available for training the models. The second approach is, despite aforementioned difficulties, to select well-defined bands and used them specifically, e.g., for minerals identification (Senthil Kumar and Rajkumar, 2014; Bosch-Reig et al., 2017; Hahn et al., 2018), for determination of soil aggregates wettability which determines water behaviour in soils (infiltration, retention) (Ellerbrock et al., 2005; Leue et al., 2010; Thai et al., 2022), or for the evaluation of qualitative parameters of soil organic matter (Gerzabek et al., 2006; Pärnpuu et al., 2022). Various types of indexes were designed to evaluate SOM aromaticity (Cunha et al., 2009; Matamala et al., 2017) or level of decomposition (Haberhauer et al., 1998; Artz et al., 2006; Matamala et al., 2017).

Presented study aims to provide an alternative to the aforementioned direct and indirect methods. It aims to introduce the applicability of infrared spectroscopy in the middle infrared part of spectra (especially diffuse reflectance infrared spectroscopy with Fourier transformation (DRIFT)) as a rapid technic with relatively simple sample preparation providing a wide range of information on soil properties applicable at complex Colluvisols description. The main effort of this paper was to propose spectral indicators usable with the same reliability for both carbonate and non-carbonate soils and to test their effectiveness in the identification of horizons of very deep colluvial soils varying in mineralogical properties, organic carbon content, and organic matter quality. This study aims to introduce an original set of relatively easy measured soil spectral parameters not requiring advanced mathematical processing or large datasets which can describe soil chemical properties, (i) qualitative (identification of the presence of certain minerals or relative comparison of the representation of different organic matter components using only spectral bands nonoverlapping with carbonate bands) and (ii) quantitative (evaluation of the amount of organic matter or carbonates in the soil using the spectra normalization by the quartz spectral band) both on the example of Colluvisols (three regions with

different lithology, climatic conditions and soil types) and (iii) determine their usefulness for defining the individual Colluvisols layers the subsequent detailed investigation of which can disentangling the complex functioning and formation history of colluvial soils.

2. Methods

2.1. Sites description

Three localities (Brumovice, Vidim, and Kosova Hora; Fig. 1) fundamentally different in their geological and pedological conditions, climate and settlement history but with similar topography were selected for this study. The naming of soil types and subtypes presented below is based on the classification (IUSS Working Group WRB, 2022).

Brumovice is situated in a loess region in South Moravia in the Czech Republic. The average annual temperature varies between 9 and 10 °C, and the average annual precipitation is between 500 and 550 mm. The history of this site and Colluvisols forming conditions are described by Zádorová et al., (2013, 2023). Soil cover is created on a Pleistocene loess layer with a variable depth ranging from several meters up to several tens of meters (Chlupáč et al., 2002). Calcic Chernozem is the original

dominant soil unit in the region, which is now gradually transforming into different soil units as a result of intensive erosion and redeposition of soil material (Jakšík et al., 2015). Areas with minimal slope (0–2°) are covered mainly by Calcic Chernozems, areas with increasing slope by its eroded forms, and the steepest parts (8–15°) of the slopes by Regosols and Calcisols. Loess itself is exposed in many cases. Colluvial soils (Kastanozems and Phaeozems (Solimovic) with deep humus horizons are formed in slope depressions (Zádorová et al., 2013). The research was performed on an agricultural parcel (area of 6 ha), forming a complex slope system with different landforms.

Vidim is situated in Central Bohemia (Czech Republic), in the Pšovka River watershed. The wider area is underlain by Cretaceous sandstones covered by a Pleistocene loess layer (Chlupáč et al., 2002). Haplic and Albic Luvisols are the original dominant soil units. The average annual temperature varies between 7 and 8 °C, and the average annual precipitation is between 550 and 650 mm. The study plot (4.5 ha of agricultural soil) is characterized by intensive topography dominated by two side valleys connected in the southwest part of the site. These two concave units represent the main accumulation positions at the plot, where colluvial soils (Haplic Luvisols (Solimovic) developed. The adjacent slopes, covered by eroded Luvisols and Regosols, are relatively
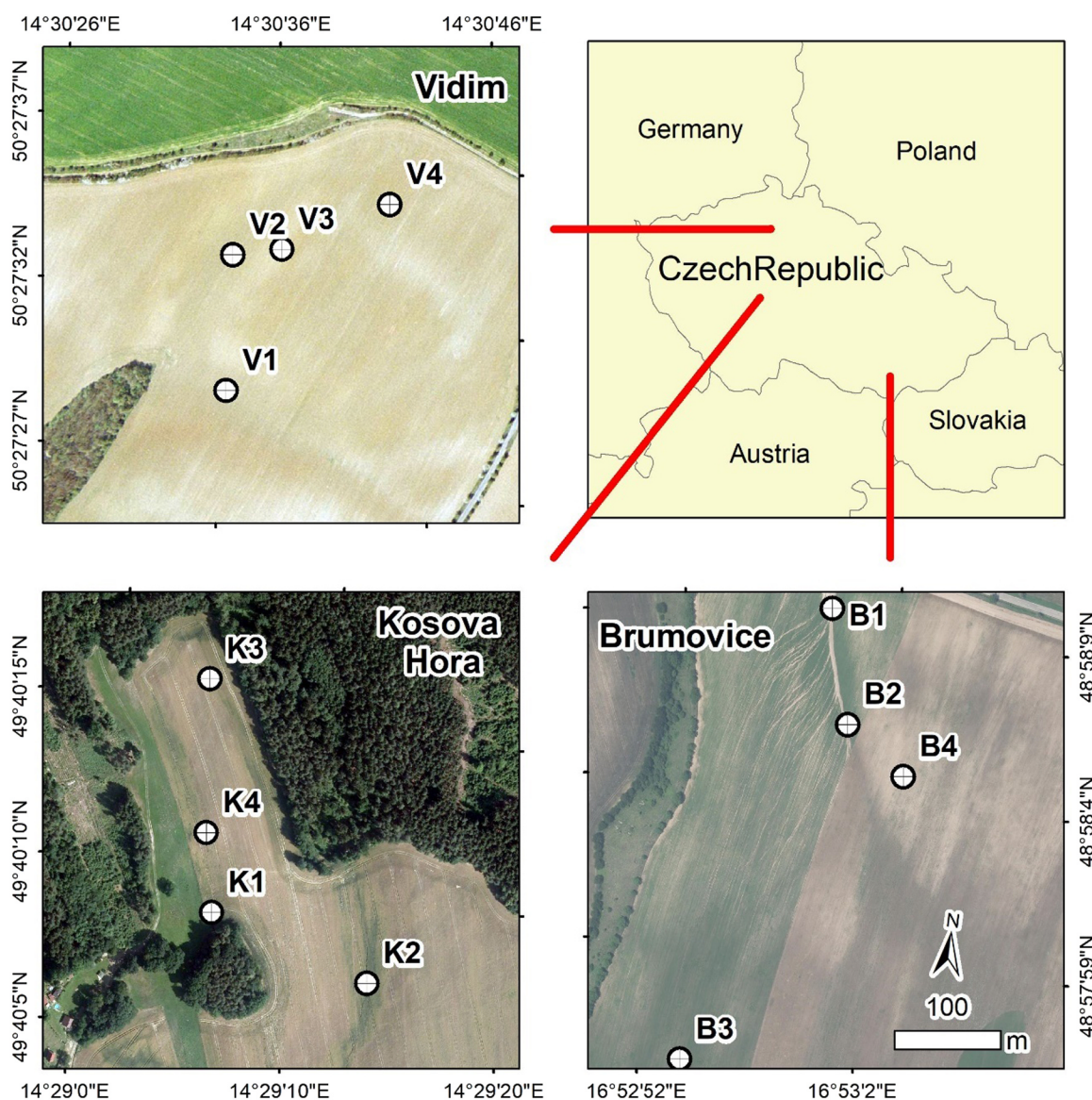

Fig. 1. Studied localities and soil pit positions.

steep (up to 12°), while the plot's south, northeast, and northwest parts are formed by flat terrain. More details about this site are given in Zádorová et al. (2014), Penížek et al. (2016), and Pavlů et al. (2022).

Kosova Hora is situated in the central part of the Czech Republic in the Central Bohemian Upland. Geologically, the area forms part of Central Bohemian magmatic pluton. The parent material of the study area derives from granodiorites, in the side valleys covered by silty deluvial sediments (Chlupáč et al., 2002). The average annual temperature varies between 7 and 8 °C and annual precipitation is between 600 and 700 mm. The study plot covers an area of 10 ha of agricultural soil. The terrain is complex comprising of backslopes, a side valley, and two significant colluvial–alluvial cones at the toe-slopes. Eutric Cambisols are the dominant soil units, significantly eroded at the slopes. Zádorová et al. (2023) described occurrence of Luvisols at the study area, namely in the flat parts of the terrain. Skeletic Leptosols occur at the steepest parts. Stratified Colluvisols (Solimovic Cambisols) developed in concave positions.

2.2. Soil sampling

Soil samples were collected from four soil pits in each area (Table 1). One pit always captures soil negligibly affected by erosion in the higher and flatter parts of the area. The second was dug in the most eroded sloping part of the area. The remaining two were located in places of accumulation of eroded material (toe-slope and side valley). Soil samples were taken every 10 cm down to the depth of the original soil-forming substrate or in-situ soil material. They were air-dried, ground, and sieved through a 2-mm sieve to analyse selected soil properties. The soil samples were ground to analytical fineness to measure the infrared spectra. For the detailed description of the field survey and selection of sampling points see Zádorová et al. (2023).

2.3. Soil chemical analyses

Soil organic carbon (SOC) content was measured using the dichromate redox titration method (Skjemstad and Baldock, 2007). $CaCO_3$ content was measured using the volumetric method corresponding to the ISO 10693 standard (08.53 calcimeter – Ejkelkamp).

Element contents (Fe_{AR}, Al_{AR}) in aqua regia extract were measured using the method of Cools and De Vos (2016). The final concentrations of Fe and Al were subsequently measured by inductively coupled plasma–optical emission spectrometry (ICP–OES) using an iCAP 7000 radial ICP emission spectrometer (Thermo Fisher Scientific Inc., USA) under standard analytical conditions.

2.4. DRIFT spectra measurement and description

MID infrared spectra were measured using the diffuse reflection technique and instrument Nicolet iS10 (Thermo Fisher Scientific Inc., USA). The spectral range was 4000–400 cm^{-1}. Before the measurement, the samples were not diluted with KBr or otherwise modified. The gold mirror was used as a background reference. The 64 scans with a resolution of 4 cm^{-1} and spectra conversion to Kubelka–Munk units were applied. OMNIC 9.2.41 software (Thermo Fisher Scientific Inc., USA) was used for spectra analysis. Well-definable bands of soil components functional groups were determined in the spectra and their reflectance converted to Kubelka–Munk units was measured.

Fig. 2 shows average DRIFT spectra of soils in all three studied regions. Description of main spectral bands of soil presents Table 2. Most of the listed spectral bands of both mineral and organic soil components can be found in all soil types. The exception are the bands of carbonates (around 2515 cm^{-1} and 1450 cm^{-1}) which are visible in the spectra only when their content is higher in the soil (approximately > 1 %). Unfortunately, the intensive band in the 1450 cm^{-1} overlaps the bands of some functional groups (1545–1500; aromatic C=C stretching, aromatic skeletal vibration, aromatic (lignin), amide II) suitable for a

Table 1

Soil profiles description and accumulation period of individual layers based on Zádorová et al. (2023).

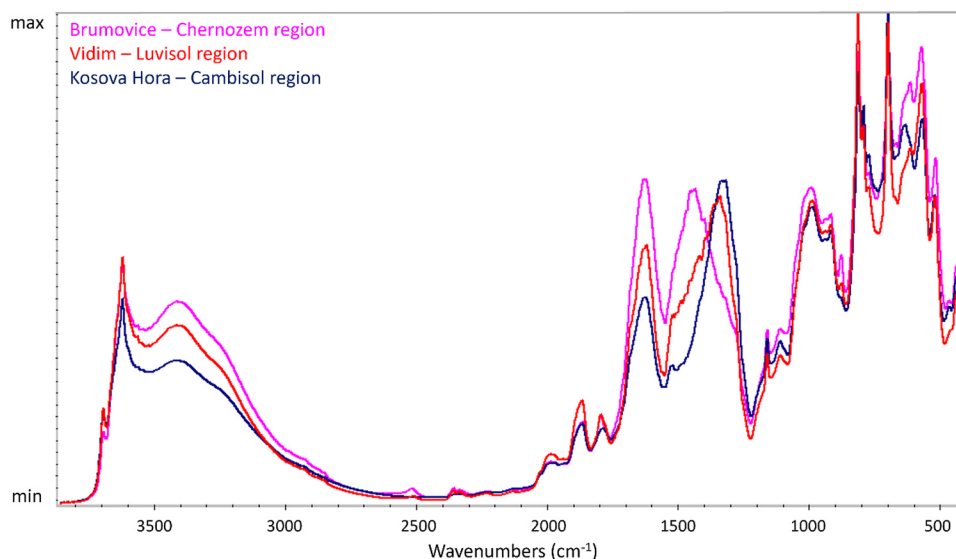| Brumovice	Layer / horizon	Depth (cm)	Period of accumulation
B1	Ap	0–25	last 30 years
Solimovic Regosol (Protocalcic, Siltic) over Calcic Chernozem	M1	25–100	last 70 years
	M2	100–150	Middle Ages
	M3	150–220	Middle Ages
	M4	220–270	Dark Ages
	M5	270–300	Late Neolithic
	2Ahb	300–350	
	2AC	350–370	
	3Ck	370–380	
B2	Ap	0–27	
Haplic Kastanozem (Siltic, Solimovic) over Calcic Chernozem (Stagnic)	M1	27–70	Middle Ages
	M2	70–120	La Tene period
	M3g	120–170	Middle Bronze Age
	M4	170–190	Early Bronze Age
	M5	190–250	Early Holocene
	2Ahgb	250–300	
	2Bwg	300–340	
	3Ckg	340–350	
B3	Ap	0–25	
Calcic Chernozem (Siltic)	Ah	25–40	
	AC	40–50	
	Ck	50–70	
B4	Ap	0–25	
Haplic Calcisol (Siltic)	Ck	25–60	
Vidim	**Layer / horizon**	**Depth (cm)**	**Period of accumulation**
V1	Ap	0–30	
Haplic Luvisol (Siltic, Cutanic, Solimovic)	M1	30–75	Late Middle Ages
	M2	75–112	Early Middle Ages
	M3	112–123	
	M4	123–160	Roman period
	M5	160–185	Roman period
	2Ahb	185–205	
	2Egb	205–220	
	2Btgb	220–240	
V2	Ap	0–30	
Haplic Luvisol (Siltic, Cutanic, Solimovic)	M1	30–55	Middle Ages
	M2	55–80	
	M3	80–92	Middle Ages
	M4	92–110	
	M5	110–170	Early Middle ages/ Dark Ages
	M6g	170–200	Early Middle ages/ Dark Ages
	2Btgb	200–220	
V3	Ap	0–37	
Calcic Luvisol (Siltic, Cutanic)	Bt	37–73	
	Bt/C	73–95	
	Ck	95–120	
V4	Ap	0–34	
Calcaric Regosol (Siltic)	C	34–80	
Kosova Hora	Layer/ horizon	Depth (cm)	Period of accumulation
K1	Ap	0–20	last 30 years
Eutric Solimovic Bathystagnic Regosol (Loamic)	M1	20–32	last 30 years
	M2	32–40	last 30 years
	M3	40–57	last 70 years
	M4	57–70	last 70 years
	M5	70–90	last 70 years
	M6	90–107	Middle Ages
	2Bg	107–120	
	3Bg	120–137	Early Holocene
	4Bg	137–180	
K2	Apg	0–27	
Eutric Solimovic Stagnic Regosol (Loamic)	M1g	27–160	Middle Ages
	M2g	160–180	Early Middle ages/ Dark Ages
K3	Ap	0–26	
Haplic Luvisol (Loamic)	Btw	26–63	
	C	63–80	
K4	Ap	0–25	
Eutric Lithic Leptosol	C	20–40	

Fig. 2. Average DRIFT spectra of soils from three studied regions in full-scale (min–max) display.

Table 2
The assignment of the major spectral bands in the soil infrared spectra (Haberhauer et al., 1998; Madejová, 2003; Vagenas et al., 2003; Leue et al., 2010; Le Guillou et al., 2015; Tinti et al., 2015).

Spectral band (cm^{-1})	Description
3700–3680	Si–O–H vibration of clays and Fe oxides (weak hydrogen bonds with the oxygens of the Si–O–Si bonds on the lower surface of the next layer)
3630–3620	Si–O–H bonds in clays and oxides (hydroxyl groups, lying between the tetrahedral and octahedral sheets)
3440–3320	O–H and H–bonded OH (mainly in organic components – alcohols, carboxyl functions, phenols)
3010–2800	aliphatic –CH$_2$ and –CH$_3$ stretching
2550–2500	carbonates
2000–1790	Si–O vibration of quartz (and 1800 calcite) overtone
1775–1711	C═O stretching in carboxylic group
1690–1570	C═O stretching of amides (amide I), H–bonded conjugated ketones, carboxyls and quinones, C═N stretching, amide II of primary amides, aromatic C═C
1545–1500	aromatic C═C stretching, aromatic skeletal vibration, aromatic (lignin), amide II
1470–1420	carbonates
1430–1300	aliphatic C–H deformation of CH$_2$ and CH$_3$ bending, C–OH deformation of COOH, C═O, and C–O stretching of phenolic groups, COO– and O–H
1160	O–Si–O in quartz
1100–1050	polysaccharides
1030–1000	Si–O of silicate stretching in feldspars and secondary alumosilicates
810 and 780	quartz doublet
695	quartz

qualitative description of the composition of soil organic matter according to, e.g., Haberhauer et al. (1998) or Cunha et al. (2009). In such cases, either a more complex preparation of the samples or mathematic peak resolve (both of which can introduce an error into the result) is necessary.

In this study, a ratio of the band around 1640 cm^{-1} and the aliphatic band (around 2930 cm^{-1}) was designed and used as an indicator describing organic matter quality (OMQ). These two spectral bands were used because they do not overlap even in carbonate soils and identify important components of SOM. Based on their ratio, the relative proportion of aliphatic, aromatic, or C═O-containing groups of SOM can be evaluated.

2.5. Normalization of the DRIFT spectra

In order to quantify the selected spectral parameters, the non-quantitative DRIFT spectra must be adjusted or normalized. Calculation of peak relative absorbances are often used. They were calculated by dividing the distinct peaks heights by the sum of the heights of all peaks and multiplying it by 100 (Gerzabek et al., 2006). In this case, we chose a different approach based more on the basic principle of soil formation. Quartz is one of the most stable minerals in the soil, and also precisely because of this, it belongs to the most abundant minerals in most soil types (Brady and Weil, 2008). The DRIFT spectrum shows the quartz bands at 1160 cm^{-1}, well-defined sharp doublet at 810 and 780 cm^{-1}, and the band at 695 cm^{-1} (Le Guillou et al., 2015). Bands of quartz are some of the most intense in the spectra of soils. They are narrow and do not overlap with others. For that reason, they were used for normalization. The spectra were normalized with the reflectance (converted to Kubelka–Munk units) of the bands at 695 cm^{-1} and 810 cm^{-1}, respectively. Both normalizations were compared. Fig. 3 shows that both normalizations return similar but not the same results. The best matches are reached in the carbonate band (2520 cm^{-1}). The
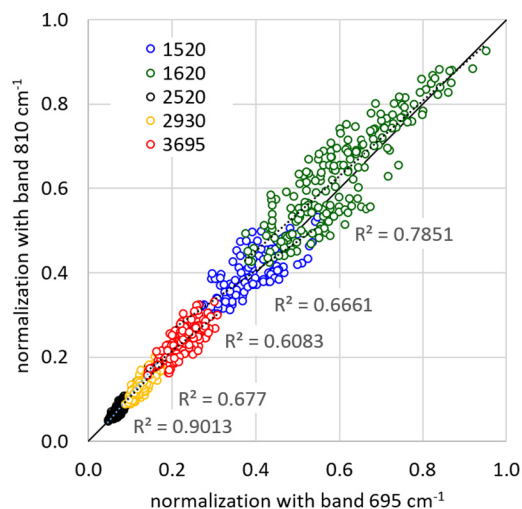

Fig. 3. Comparing of two types of spectra normalization. Coefficients of determination (R^2) was computed separately for selected spectral bands. Black full line indicates theoretical 1:1 relationship.

selection of a more appropriate type of normalization was therefore further tested using basic soil properties.

The heights of peaks in the normalized spectra were correlated with the soil parameters measured by standard analytical methods (Table 3). STATISTICA 13.3 software (StatSoft Inc., USA) was used to perform correlation analysis. The heights of spectral peaks, whose shapes and intensities were not affected by the presence of carbonates, were included in the correlation analysis for all samples (N 195). The values affected by the presence of carbonates were excluded from the analysis (N 120), therefore, the correlation coefficients in such cases are valid only for samples with zero or very low carbonate content. Table 3 documents that better results (higher correlation coefficients) can be achieved when normalizing with the 810 cm^{-1} band.

3. Results and Discussions

3.1. Using DRIFT normalized spectra as soil chemical parameters predictors

In addition to the more appropriate type of normalization, the correlation analysis also indicated which soil parameters can be derived on the base of normalized spectra. SOC content correlate significantly with all spectral parameters belonging SOM (2925, 2850, 1620, and 1512 cm^{-1}). The highest correlation was found for SOC and sum of all SOM peaks heights. The disadvantage of this spectral parameter is its unsuitability for carbonate soils, where two (2850 and 1512 cm^{-1}) of the four bands used are deformed or covered by a band of carbonates. With regard to all types of soil, it appears to be the most suitable band of organic substances (1620 cm^{-1}).

Carbonates appear in two bands in IR spectra (around 2515 cm^{-1} and 1450 cm^{-1}). The first of these is well isolated from the other bands and, although it is less intense than the second mentioned, is well identifiable and measurable. The 1450 cm^{-1} band is located in the fingerprint area, it is very intense, but as an easy usable parameter it is unsuitable due to the number of overlaps. Very high correlation was found for CaCO$_3$ content and 2515 cm^{-1} peaks heights.

Two well defined peaks (3690 and 3620 cm^{-1}) belong, according to the literature (Madejová, 2003; Le Guillou et al., 2015; Tinti et al., 2015), to the vibration of clays (alumosilicates) and Fe oxides. Each peak individually correlates with aluminium and iron contents. However, higher correlation coefficients were achieved after summing the heights of both evaluated peaks.

The possibility of predicting soil parameter values from normalized DRIFT spectra was tested using simple regression analysis. Predictive models for estimating the SOC, CaCO$_3$, Al$_{AR}$ and Fe$_{AR}$ concentrations in soil separately for studied areas and soil regions was designed. The coefficients of determination (R^2), root mean squared error of prediction (RMSEP – the differences between predicted and observed values quantifying the accuracy of the prediction by comparing the prediction errors of different models), and residual prediction deviation (RPD – the standard deviation of observed values divided by the RMSEP) were calculated to verify the model quality (Table 4). The RPD considers both prediction error and variation in observed values, resulting in a model validity metric that is objective and easily comparable across model validation experiments (Williams and Sobering, 1993). The result shows that carbonate content in the Chernozem and Luvisol regions is the best-predicted soil property (high R^2 and low RMSEP; range of CaCO$_3$ content 0–25 %). A specific situation is in the Cambisol region where CaCO$_3$ concentrations are zero or very low (max = 0.07 %), resulting in low RMSEP but also very low R^2. The prediction of carbon concentration from FTIR spectra is well known (Barra et al., 2021) and the larger and more diverse the dataset, the more accurate is the prediction. In this case, we are working with a limited dataset with relatively low variability in organic carbon content (min = 0.06 %; max = 1.90 %). Accordingly, the organic carbon content is better predictable if data from all regions are used, although there is often less RMSEP and RPD in models from individual regions. Better results were obtained using more spectral bands of soil organic components. In this case, samples with a higher carbonate content had to be excluded from the calculations, as some of their bands overlap bands of organic soil components, as mentioned above. Predictions of Al$_{AR}$ and Fe$_{AR}$ contents are the most accurate (highest R^2 and lowest RMSEP) for the Luvisol region. However, even there their coefficients of determination are relatively low.

3.2. Application of normalized DRIFT spectra in Colluvisols description

From the results published also by Zádorová et al. (2023) and used there for comparison with spectral parameters (Figs. 4–6) it is evident that SOC concentrations are very low in soils of all these localities. SOC content is only higher in the Chernozem region – Brumovice (maximal values of SOC content: 1.8 % in the oldest sediments, 1.5 % in the Ap horizon, respectively) than in others (Vidim – Ap – 1.2 %; Kosova Hora – Ap – 1.1 %). Cambisol region differs from others in higher content of Al$_{AR}$ and Fe$_{AR}$ as elements abundant mainly in B horizons and in their almost zero carbonate content, unlike soils formed on loess (Chernozem and Luvisol region), where in some layers carbonate content reaches up

Table 3

Correlation coefficients identifying relationships among basic soil characteristics and spectral bands (computed normalized band height or sum of these heights; Σalif – sum of 2925 and 2850 band heights; Σorg – sum of 2925, 2850, 1620, and 1512 band heights; Σclay – sum of 3690 and 3620 band heights).

Band (s)	NB$_{3690}$	NB$_{3620}$	NB$_{2925}$	NB$_{2850}$	NB$_{2515}$	NB$_{1620}$	NB$_{1512}$	Σalif	Σorg	Σclay
N	195	195	195	120	195	195	120	120	120	195
normalization with band 695 cm^{-1}										
SOC	−0.265 ***	0.260 ***	0.476 ***		−0.064	0.711 ***	0.440 ***	0.551 ***	0.701 ***	0.112
CaCO$_3$	−0.406 ***	−0.127	0.072	0.178	0.850 ***	0.098	0.197 *	0.211 *	0.275 **	−0.228 **
Al$_{AR}$	0.332 ***	0.330 ***	−0.049	−0.014	−0.324 ***	−0.195 **	−0.542 ***	0.008	−0.272 **	0.359 ***
Fe$_{AR}$	0.294 ***	0.383 ***	−0.050	−0.047	−0.314 ***	−0.157	−0.525 ***	−0.019	−0.246 **	0.387 ***
normalization with band 810 cm^{-1}										
SOC	−0.252 ***	0.277 ***	0.485 ***	0.384 ***	−0.057	0.757 ***	0.611 ***	0.444 ***	0.801 ***	0.130
CaCO$_3$	−0.193 **	0.113	0.273 ***	0.097	0.885 ***	0.315 ***	0.210 *	0.122	0.260 **	0.023
Al$_{AR}$	0.532 ***	0.497 ***	0.088	0.214 *	−0.215 **	−0.096	−0.386 ***	0.226 *	−0.041	0.558 ***
Fe$_{AR}$	0.441 ***	0.509 ***	0.050	0.127	−0.224 **	−0.082	−0.426 ***	0.145	−0.071	0.537 ***

*, **, *** Significant at the probability level 0.05, 0.01, and 0.001, respectively; correlation coefficients of later discussed (3.1) relationships are in red.

Table 4
Linear regressions models and their coefficients of determination (R^2), root mean squared error of prediction (RMSEP), and residual prediction deviation (RPD). NB – normalized band height; Σorg – sum of 2925, 2850, 1620, and 1512 band heights; Σclay – sum of 3690 and 3620 band heights.

	N	regression equation	R^2	RMSEP	RPD
All sites	195	$SOC = 2.880(NB_{1620})$* ** $- 1.172$ * **	0.574	0.302	1.532
Chernozem region	85	$SOC = 3.370(NB_{1620})$* ** $- 1.540$ * **	0.368	0.354	1.258
Luvisol region	58	$SOC = 2.769(NB_{1620})$* ** $- 1.102$ * **	0.339	0.288	1.170
Cambisol region	46	$SOC = 2.056(NB_{1620})$* ** $- 0.751$ * *	0.272	0.212	1.171
all sites	120	$SOC = 2.000(\Sigma org)$* ** $- 1.818$ * ***	0.641	0.319	1.669
Chernozem region	35	$SOC = 1.342(\Sigma org)$* ** $- 0.639$	0.441	0.262	1.451
Luvisol region	39	$SOC = 1.922(\Sigma org)$* ** -1.714 * **	0.445	0.251	1.343
Cambisol region	46	$SOC = 0.842(\Sigma org)$* ** $- 0.655$ * *	0.322	0.204	1.214
All sites	195	$CaCO_3 = 168.8(NB_{2515})$* ** $- 11.28$ * **	0.787	2.276	2.155
Chernozem region	85	$CaCO_3 = 191.6 (NB_{2515})$ * ** $- 13.16$ * **	0.885	2.023	2.951
Luvisol region	58	$CaCO_3 = 166.2(NB_{2515})$* ** $- 9.892$ * **	0.876	1.323	2.706
Cambisol region	46	$CaCO_3 = -0.500(NB_{2515})$* $+ 0.066$ * **	0.099	0.041	0.498
Cher.+Luv. Regions	131	$CaCO_3 = 175.2(NB_{2515})$* ** $- 11.14$ * **	0.879	1.980	2.691
All sites	195	$Al_{AR} = 23892(\Sigma clay)$* ** $- 4187$ *	0.310	3837	1.205
Chernozem region	85	$Al_{AR} = 10898(\Sigma clay)$* ** $+ 5139$	0.092	2467	1.050
Luvisol region	58	$Al_{AR} = 19531(\Sigma clay)$* ** $- 2224$	0.572	2345	1.455
Cambisol region	46	$Al_{AR} = 40453(\Sigma clay)$* ** $- 13662$ * *	0.493	5051	1.405
All sites	195	$Fe_{AR} = 21471(\Sigma clay)$* ** $+ 1007$	0.289	3629	1.186
Chernozem region	85	$Fe_{AR} = 9641(\Sigma clay)$* $+ 9884$ * *	0.048	3101	1.025
Luvisol region	58	$Fe_{AR} = 18706(\Sigma clay)$* ** $+ 2036$	0.550	2346	1.419
Cambisol region	46	$Fe_{AR} = 34012(\Sigma clay)$* ** $- 6684$	0.440	4727	1.337

* , * *, * ** Significant at the probability level 0.05, 0.01, and 0.001, respectively.

to 25 %.

Normalized spectra are presented as soil profile spectral maps (Figs. 4–6). These maps are supplemented with data of measured soil characteristics in the corresponding layers. The maps mainly show variability in the height/intensity of the normalized bands of OH groups (3440–3320 cm^{-1}), bands of organic substances (1690–1570 cm^{-1}), and bands of carbonates (1470–1420 cm^{-1}). This intensity corresponds very well with the measured soil properties. The z-axis scale is set so that the map best captures the variability of these intense bands. Less intense bands of aliphatic groups or carbonates in the region 2550–2500 cm^{-1} are therefore less visible. In general, it can be stated that this form of spectrum processing/visualization documents changes in soil properties along the depth gradient and can help in the identification and description of the individual layers of the Colluvisols discussed below.

In addition, spectra can also provide information on the qualitative parameters of soil organic matter, in this case, represented as OMQ index. Based on this ratio, the relative proportion of aliphatic, aromatic, or C=O-containing groups of SOM is evaluated. This proportion determines the mobility or stability of SOM through these components' affinity for soil minerals and for water. Aromatic compounds are less mobile, therefore, they are likely retained in the mineral soil horizon (Bi et al., 2013). Aromatic and aliphatic acids, such as for example lignin monomers, appear to be selectively retained on mineral surfaces and polysaccharides and protein appear to be selectively preserved in organo-metallic complexes (Angst et al., 2021). Absorption bands at 2921 and 2852 cm^{-1} indicate the hydrophobic (alifatic) groups of SOM and at the 1630 cm^{-1} hydrophilic groups (aromatic and C=O groups (O and N containing hydroxyl and carboxyl groups)). Aromatic rings, generally assumed to indicate hydrophobic groups, can show hydrophilic properties if they are conjugated with C=O groups (Ellerbrock et al., 2005; Leue et al., 2010). SOM richer in aromatic, alkyl, and carboxyl groups, but containing lower amounts of hetero-alkyl groups can be considered as more humified and chemically mature. Conversely, a lower number of aromatic groups and a higher percentage of O, N-alkyl C, predominantly in carbohydrate and polypeptide structures, represents a lower degree of humification and chemical maturity (Maryganova et al., 2010).

It has been shown, that aromaticity of organic matter increases in the common intact soil profiles with degrees of decomposition, maturity of OM and generally with depth (Veum et al., 2014; Margenot et al., 2015; Thai et al., 2021). The profiles of Colluvisols are specific and the quality of organic matter can vary depending on the sedimentation history of the layers and the origin of the sedimented material. Soil burial can isolate organic matter from the atmosphere, creating environmental conditions unfavorable to microbial decomposition, which can lead to the persistence of SOC relatively unchanged for thousands of years and conversely once exposed to ambient conditions, soil microbial activity can recover to rates comparable to surface soils (Chaopricha and Marín-Spiotta, 2014). And it is precisely this variability that the OMQ index can capture well.

In the Chernozem region (Fig. 4), the deepest Colluvisols were found with the aggregate thickness of colluvial layers exceeding 300, resp. 250 cm in the profiles B1 and B2. Buried profiles of former Chernozems were identified below the colluvial material (Zádorová et al., 2023). Chernozems are characterized by a thick very dark-coloured chernic surface horizon (Ah) passing into a light-coloured soil-forming substrate rich in carbonates (Ck) (IUSS Working Group WRB, 2022). Sharp change in CaCO$_3$ content between recent or buried Ah horizon and loess is evident in the B1 and B3 (less evident in the B2) spectral maps, both in the band 1470–1420 cm^{-1} and 2550–2500 cm^{-1}. The buried Ah horizons and oldest sedimented layer M5 in B1 profile and M3–5 in B2 profile are almost decalcified. Layers M4(B1) and M2(B2) are in spectral map defined by gradual transition and CaCO$_3$ content increase. In the spectral maps, medieval colluvial layers (B1 – M3 and M2) and recently deposited layers (B1, B2 – M1 and Ap) with high CaCO$_3$ content are well identified. These layers reflect accumulation of material transported from truncated source profiles, such as B4 (Zádorová et al., 2023) and represent a long-term erosion process and soil degradation in a landscape of south Moravia Chernozem region (Jakšík et al., 2015; Sarapatka et al., 2018).

Intensity of spectral band around 1620 cm^{-1} well describes the distribution of organic matter in soil profiles. Orange and red colours correspond to the buried Ah horizon and oldest sedimented layer M5 in B1 profile and to M5 and M4 layers in B2 profile. In the B1 profile the organic matter distribution is also reflected in broad band of OH vibrations in the range 3500–3300 cm^{-1}. The vibration of the OH group belongs mainly to organic components — alcohols, carboxyl, and phenols, as was mentioned in Table 1 (e.g., Tinti et al., 2015). Different situation is in B2 profile where this band is similarly intense in whole profile, including layers with very low SOM content. A wider band of OH groups in the case of these layers may correspond to higher contents of minerals belonging to (oxy)hydroxides (Madejová, 2003; Tinti et al.,
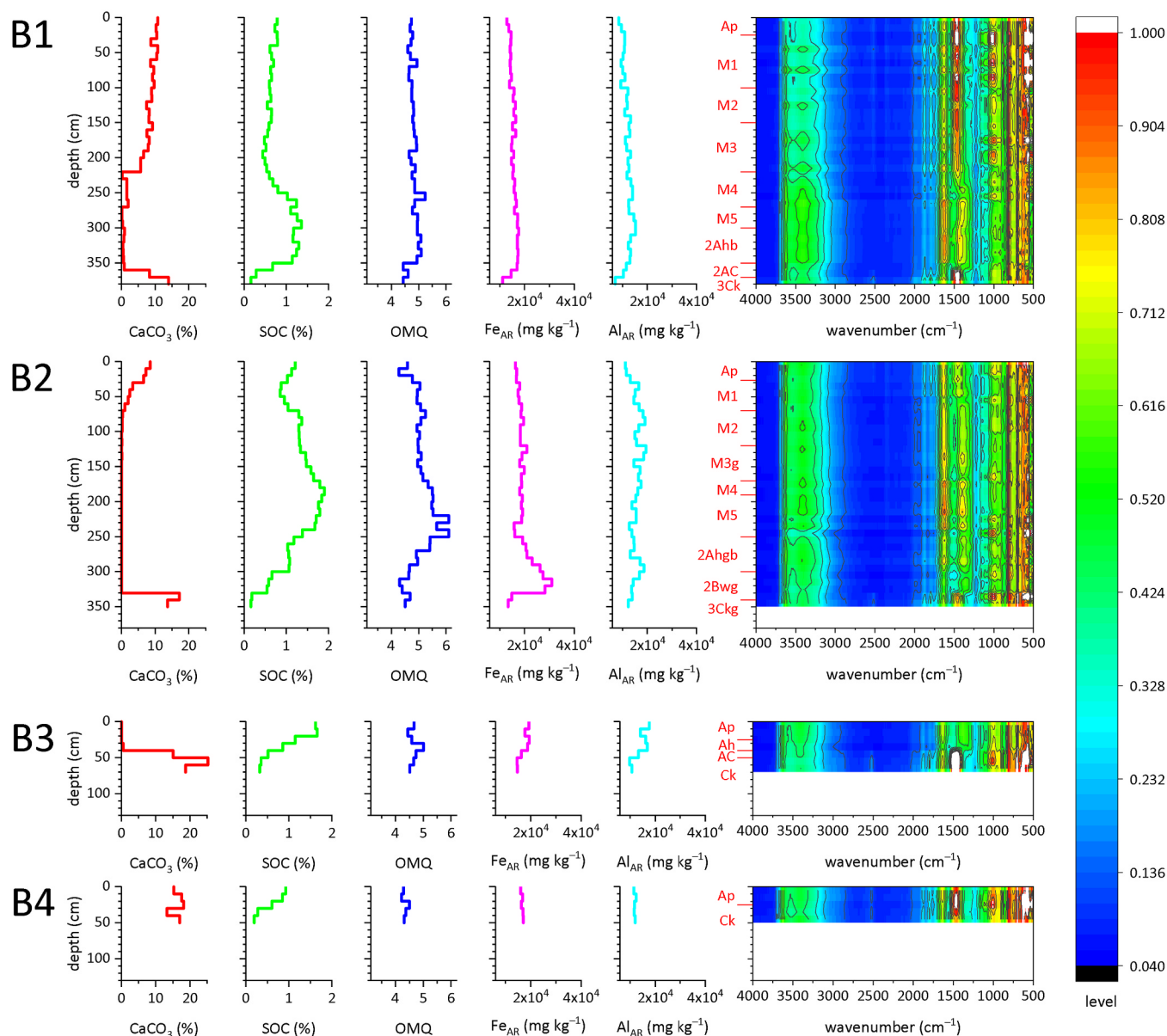
Fig. 4. Brumovice – Chernozem region – soil profiles distributions of CaCO$_3$ and SOC contents, organic matter quality (OMQ) index, Fe$_{AR}$ and Al$_{AR}$ contents, and spectral maps after spectra normalization by band 810 cm^{-1}.
Soil horizons description is adopted from Zádorová et al. (2023).

2015). Zádorová et al. (2023), who presented mineralogical composition of these soil profiles, identified the highest goethite (FeO(OH)) abundance in 2Bwg (B2) horizon. Also Fe$_{AR}$ concentration in this horizon is higher than in other parts of B2 profile. Band of OH group is relatively intense there, but 1620 band of organic matter is weak. These two pieces of information together can therefore indicate the presence of OH groups in the mineral components of the soil. On the contrary, if the content of (oxy)hydroxides in the soil profile does not change (such as in B1), the band of OH groups can indicate the amount of organic matter.

Quality of organic matter is documented by OMQ index. The higher the ratio, the higher is the relative proportion of aromatic and C═O-containing groups of SOM (and relative proportion of aliphatic groups of SOM is lower). In general, the values of this index higher in the Chernozem region (compared mainly to the Cambisol regions) and the highest are in the Ah horizons or in oldest sediments. The highest values of this index were found in M5 layer of B2 horizon. Accumulation of this colluvial layer falls into the Early Holocene period (7940 ± 500 years BP) (Zádorová et al., 2023) and the deposition of exclusively humic

material from the chernic horizons of the source soils is assumed. The organic matter with the lowest proportion of aliphatic components occurs at a depth of 230–250 cm. From this point of view, it can be characterized as stable and relatively recalcitrant and very resistant to decomposition (Maryganova et al., 2010; Bi et al., 2013; Angst et al., 2021). The values of this index are lower in the Ap horizons or recent sediments of all the studied profiles, which proves the presence of fresher, less stabilized organic matter richer in aliphatic components, e. g., polysaccharides, proteins, aliphatic organic acids, etc.

Like the previously discussed Chernozems, Luvisols also developed on loess but only after previous decalcification of the upper parts of the soil profile. Carbonates bands in ranges 1470–1420 cm^{-1} and 2550–2500 cm^{-1} are therefore the most obvious in Ck horizon of V3 profile. Furthermore, they are visible in profile V4, where confirmed difference between Ap (higher CaCO$_3$ content) and C horizon. The only band in range 1470–1420 cm^{-1} is partially displayed in V2 profile as extension band around 1300 cm^{-1}. This extension is evident from M3 layer to soil surface. Higher CaCO$_3$ contents appeared in the soil
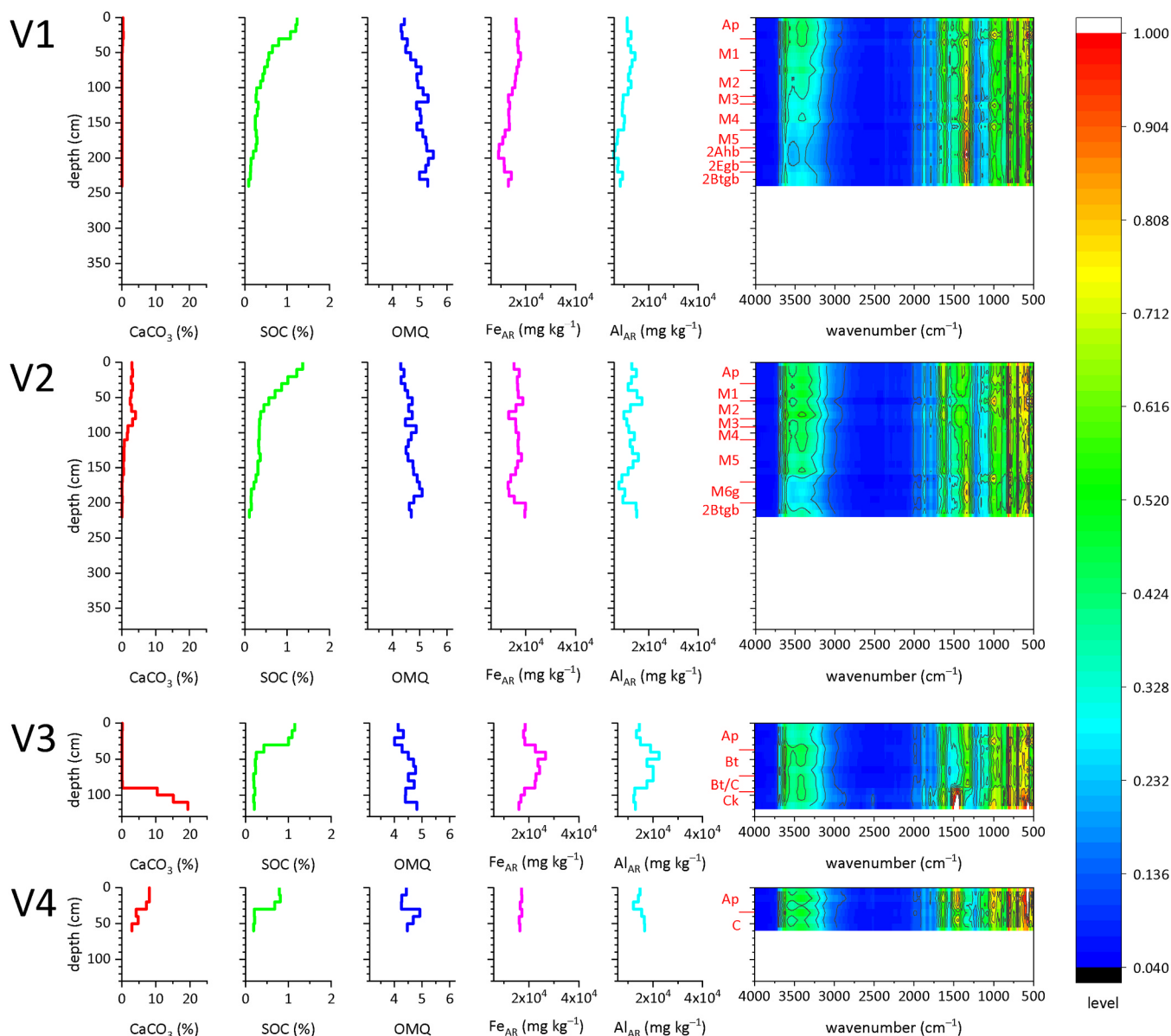
8

Fig. 5. Vidim – Luvisol region – soil profile distribution of CaCO₃, SOC, organic matter quality (OMQ) index, Fe_AR and Al_AR contents, and spectral maps after spectra normalization by band 810 cm⁻¹.

sediments document significant truncation of source Luvisols and admixture of exposed loess (Loba et al., 2023). Carbonates contents below 5 % are no longer reflected in the area 2550–2500 cm⁻¹ of spectral maps.

The content of SOC continuously decreases with depth in V1 and V2 profile. It is documented in decreasing 1640 cm⁻¹ band intensity in their spectral maps. A more pronounced change in the SOC content in the V3 and V4 profiles forming a lower boundary of Ap horizon was manifested in this band only in the V4 spectra.

The vibration of the OH group, similarly to Brumovice locality, belongs to organic matter and to (oxy)hydroxides. Even though their affiliation is variable, specific layers can be defined based on them in spectral maps. In the case of V1 profile, Ap horizon with higher SOC content and 2Ahb horizon with low SOC, Fe_AR and Al_AR contents are identifiable. Similar situation (as in 2Ahb) is in M6g layer of V2 profile. In the V3 profile, effect of mineral soil phase is dominant and OH groups band is the most intense in horizons Bt and Bt/C with the highest Fe_AR and Al_AR contents. Higher Fe_AR and Al_AR contents are reflected in two narrow peaks (3690 and 3620 cm⁻¹) belonging to vibration of clays

(alumosilicates) and Fe oxides (Madejová, 2003; Le Guillou et al., 2015; Tinti et al., 2015). It is their narrowness and the resolution of the spectral map that limits their applicability in identifying individual layers.

Organic matter quality is comparable with Chernozem region. OMQ index varies between 4 and 5.5. The lowest values well indicate Ap horizon in all four profiles. Recent soil management and fresh organic material impute is documented by higher organic matter content with a higher proportion of aliphatic functional groups, which can be found in polysaccharides, proteins, aliphatic organic acids, etc. In the deeper parts of soil profiles, where SOC content is low, OMQ reach the highest values. It could be similarly as in Chernozem region caused by the firm binding of organic matter to the mineral component of the soil and its maturity and resistance to decomposition, which is influenced by the hydrophobicity of its aromatic components (Leue et al., 2010; Maryganova et al., 2010; Bi et al., 2013; Angst et al., 2021). In the case of V1 profile, the high OMQ values appertain to 2Ahb horizon, in V2 profile to M6g respectively. Obvious quality change is documented in V3 and V4 profile at the lower boundary of Ap horizon.
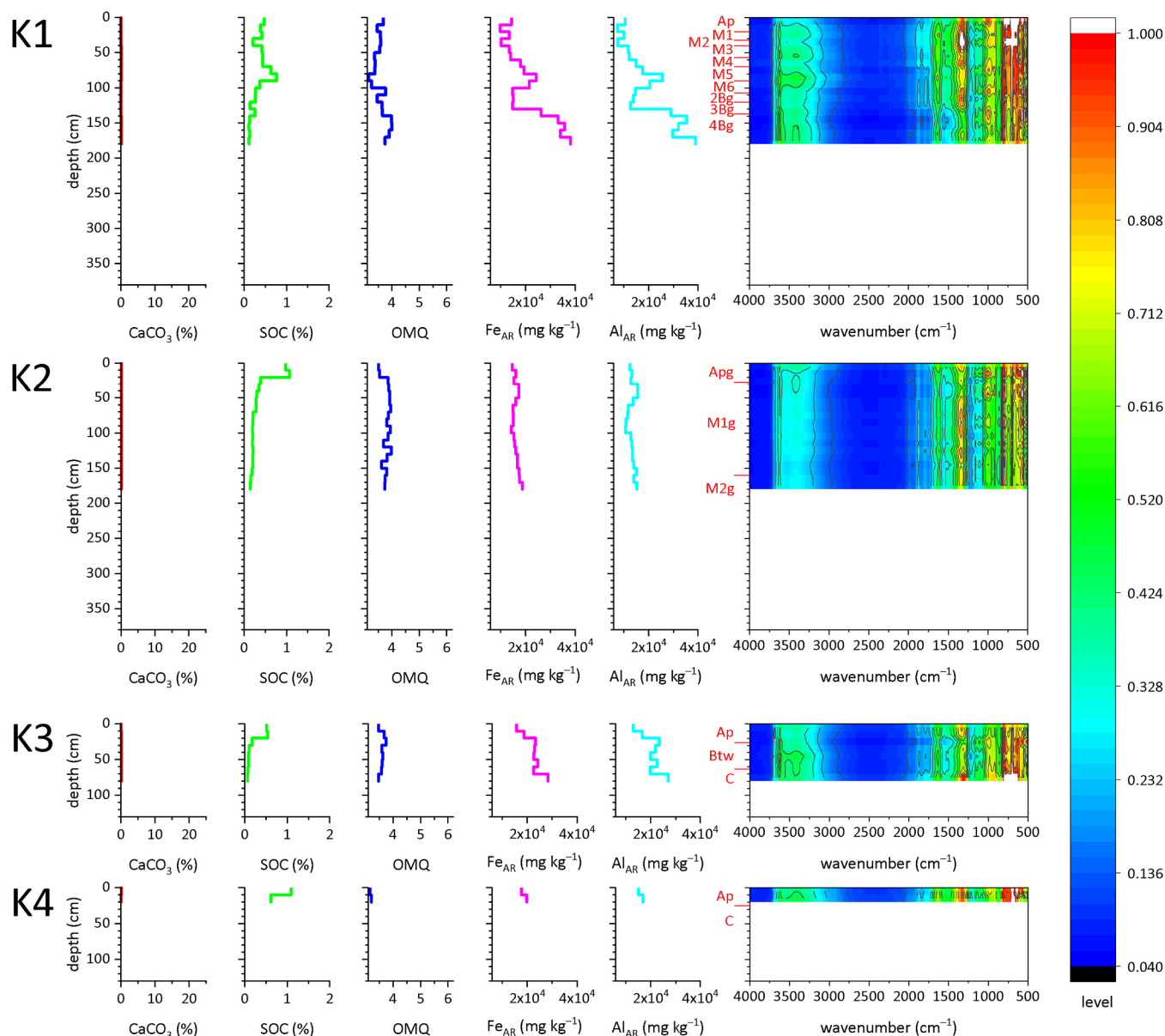
Fig. 6. Kosova hora – Cambisol region – soil profile distribution of $CaCO_3$, SOC, organic matter quality (OMQ) index, Fe_{AR} and Al_{AR} contents, and spectral maps after spectra normalization by band 810 cm^{-1}.
Soil horizons description id adopted from Zádorová et al. (2023).

Soils of Kosova Hora area are characterized by very low or no carbonate content. They contain a tiny amount of organic matter in the soil profile. In the K1 profile, maximal SOC content (0.76 %) was identified in a depth of 90 cm, while it peaks in topsoil of K2, K3 and K4 profiles. While maintaining the same scale as for Chernozems and Luvisols, only a few differences between the individual layers can be seen in the spectral maps. Bands of iron oxides and aluminosilicates (3690 and 3620 cm^{-1}) are more prominent here, which corresponds to the character of Cambisols given by their pedogenesis. Transformation of parent material should be evident from the formation of soil structure, mostly brownish coloration and increasing clay percentage. Cambic horizons also usually show higher oxide and/or clay contents than the underlying layer (IUSS Working Group WRB, 2022). In the locality, however, the situation is complicated by the mixing of other materials, mainly loess-like silty sediment and clayey material, into the granodiorite eluvium. In addition to significant weathering, the micromorphological record also revealed relatively well-developed clay coatings in Btw horizon (K3) and 4Bg (K1), not very typical for this area, representing a transition from Cambisols to Luvisols (Zádorová et al., 2023). This is consistent with the higher content of aluminosilicates and iron oxides in the Btw horizon (K3), which is also evident from the intensity of the normalized bands 3690 and 3620 cm^{-1}.

The most striking differences can be seen in the wide band of OH groups. A pair of layers M5 and M6 is well identifiable in the K1 soil profile. There are relatively high contents of SOC, Fe_{AR} and Al_{AR}. Zádorová et al. (2023) attributed an increase of different compounds (not only SOC, but also human-bound substances) in M5 layer to the higher precipitation and erosional activity in 1960's and later stabilization of the layer. The deepest layers (3Bg and 4Bg of this profile), dated to Early Holocene, with the highest Fe_{AR} and Al_{AR} contents are also separated from others in this vibration band and their very low SOC content is manifested in low intensity of 1620 cm^{-1} band too. Iron and aluminium contents are relatively constant in K2 profile and that is why the Apg horizon richer in organic matter is clearly visible here in the band of OH groups.

It can be said that the soil organic matter in this region contains a

higher proportion of aliphatic components than the organic matter of Chernozems and Luvisols. OMQ index values varies between 3 and 4. Low values are in Ap horizons of K2 and K4 soil profiles. Interestingly, the organic matter of profile K1 in a depth of 90 cm (M5) has the least aromatic components, whereas the SOC content is the highest. Stability and resistance of organic matter is based on organic matter chemical composition but also (and probably mainly) on organic matter interactions with soil minerals. SOM is stabilized by two mechanisms: by the formation of mineral-associated organic matter and by the formation of aggregates (Angst et al., 2021). Higher proportion of aliphatic groups in the stable soil aggregates was present by Thai et al. (2022). Polysaccharides and proteins as aliphatic components of SOM with affinity to organo-metallic complexes formation was present by Angst et al. (2021). Thus, it is possible that the stabilization (of otherwise relatively mobile organic matter) is caused by binding to iron oxyhydroxides. Positive effect of iron forms on aggregates stability was found by Pavlů et al. (2022) exactly in this region.

4. Conclusions

We showed the possibility of identifying differences among Colluvisols layers using DRIFT spectroscopy. For testing, a specific environment with significant erosional redistribution and complex soil development was used, where sedimentary layers of different ages and in-situ formed soils were combined. The three localities were chosen from three different soil-climatic regions. As the primary aim was to demonstrate the method described above, we didn't attempt to explain in detail the causes of the differences in the individual colluvial layers or to describe the history of their development in a landscape context.

We can conclude that the set of spectral parameters based on normalization using quartz spectral bands and organic matter quality evaluation using the newly designed OMQ index based on the ratio of bands (aliphatic compounds spectral bands ($2930~\mathrm{cm}^{-1}$) and aromatics and $C{=}O$ groups band around $1640~\mathrm{cm}^{-1}$) reflectance is a beneficial tool for the description of soil parameters. It is equally suitable for non-carbonate soils as well as for soils with higher carbonate contents, which otherwise usually cause difficulties in the interpretation of SOM spectral parameters. It does not require complicated and time-consuming sample preparation, provides a comprehensive view of the soil and its mineral and organic components, and can provide information that is difficult to measure with other methods. From the perspective of quantifying some soil components, this method does not provide absolutely accurate results. The best results were obtained when predicting the carbonate content in Chernozem and Luvisol regions (R^2 was 0.89 and 0.88, respectively; range of $CaCO_3$ content 0–25 %). The amount of organic carbon was predicted from such normalized spectra with less confidence ($R^2 = 0.64$) because of the relatively low variability of organic carbon content in the studied soils (min = 0.06 %; max = 1.90 %). However, it can be used to define areas or soil horizons with similar parameters and thus limit the number of samples analysed by more precise and sophisticated methods. OMQ is another indicator that helps to identify and describe individual colluvial layers. The highest values of this indicator were found in in the Chernozem region (> 6, while, e.g., in the Cambisol region is < 1), especially in the layers corresponding to the oldest sediments or buried in-situ horizons. This means that there is organic matter with the lowest proportion of aliphatic components, which can be characterised as stable and relatively recalcitrant and very resistant to decomposition. In the Cambisol region, the organic matter contains a higher proportion of aliphatic components than the organic matter of Chernozems and Luvisols. Iron oxyhydroxides contribute to its stabilisation in the soil and the spectral band related to OH groups of these oxyhydroxides has also been used to identify the buried B horizon of the Cambisols.

Finally, infrared spectroscopy is a relatively inexpensive method of analysis, and the aforementioned limitation on the number of samples for more specific analyses can mean a significant reduction in the cost of soil survey.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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7.5. Changes in the composition of soil organic matter after the transformation of a natural beech stand into a spruce monoculture. (Under review)

Thai, S., Pavlů, L., Vokurková, P., Thet, B., Drábek, O., Vejvodová, K., Tejnecký, V. (2024). Changes in the composition of soil organic matter after the transformation of a natural beech stand into a spruce monoculture. Journal of Soil and Water Conservation (under review).

1   **Changes in the composition of soil organic matter after the transformation of a natural beech stand into a**

2   **spruce monoculture**

3   **Abstract**

4   The compositions of soil organic matter are considered a key influence on C sequestration and global climate

5   change and can be associated with the changes in vegetation cover in the terrestrial ecosystem. Our study aimed

6   to evaluate the chemical soil structures and the various organic components from available or reactive to more

7   stable forms in forest soils (beech and spruce) affected by acidification and after conversion from a fairly close to

8   natural beech stands to spruce monoculture. The soil samples were collected in each horizon: litter horizons (L),

9   fermented horizons (F), humified horizons (H), organo-mineral horizons (A), and subsurface mineral horizons (B).

10   The soil pH, cation exchange capacity, total soil organic carbon, dissolved organic carbon, and detailed low

11   molecular mass organic acids speciation in water extract were measured. Thermal analysis with continued heating

12   was performed to analyze the stability of soil organic matter. Alkaline extractable organic substances (AEOS)

13   were separated to identify the chemical soil structures using infrared spectroscopy. Our results showed that beech

14   stands exhibited higher dissolved organic carbon and low molecule mass organic acid contents than spruce stands.

15   The evaluation with thermal analysis found the Tmax values ranged from 400 to 500°C under both forest stands.

16   The aliphatic CH groups within soluble AEOS gradually disappeared with deeper soil horizons under both forest

17   species, while the aliphatic groups in low soluble AEOS were more pronounced in A horizon under spruce and

18   relatively increased with depth under beech stands. The carboxylic groups were more prevalent in deeper soil

19   horizons, while polysaccharide chains, as well as nitrogen functional groups, decreased with depths under both

20   forest stands but were more prevalent under beech than spruce stands. These findings suggest that the stability of

21   organic matter through the forest soil profiles increased due to transformation of various organic compounds from

22   litter to more stable organic matter with higher amounts of lignin components to greater amounts of carboxylic

23   groups and aromatic groups in deeper soil horizons. Furthermore, a higher proportion of mobile component of soil

24   organic matter and acidic COOH, together with lower pH and cation exchange capacity under spruce, result in

25   leaching of nutrients, releasing risk elements into soil solution, and accelerating podsolization process. Therefore,

26   changes in vegetation cover caused changes in the qualitative composition of soil organic matter throughout the

27   forest soil profile and had relevant consequences on fundamental soil function and services such as biogeochemical

28   nutrient cycling and carbon stock.

29   **Key words:** Forest soil−infrared spectroscopy−organic matter composition−Podzols−Cambisols

Introduction

Soil organic matter (SOM) is the primary component presented in the soil and plays essential roles in regulating the nutrient cycle, adsorption and desorption processes, and especially carbon stabilization (Ohno et al. 2009). SOM is a mixture of components with different molecular weights, polarities, and functional groups that could maintain the mobility of contaminants in the soil (Ukalska-Jaruga et al. 2019). The quality and quantity of SOM consist differently in the terrestrial ecosystem due to plant residue decomposition, the surrounding environmental conditions (temperature and precipitation), and especially the influences of the different forest species (Ribeiro et al. 2001; Lal 2018). For instance, the tree species affect the SOM in various ways such as bulk deposition, interception, canopy uptake and leaching, stemflow, nutrient uptake, and organic acids exudation (Bradová et al. 2015; Habumugisha et al. 2018). On the other hand, the residues found in spruce forests tend to decompose slowly resulting in SOM stabilization, while the residues found in beech are rapidly decomposed resulting in the nutrient availability for the plants (Nacke et al. 2016; Richardson and Friedland 2016; Campbell and Paustian 2015). Characterization of SOM quality is crucial due to its implications in SOM permanence, which can greatly affect main issues related to global climate change such as carbon sequestration or the vulnerability of current SOM stocks to disturbance (Fernández et al. 2011).

Recently, the stable part of SOM has been ascribed in the new perception as a supramolecular aggregate, which bridges the functional groups of the molecule and could protect the high quality of organic compounds by the strong bond to metals and clays (Clarholm et al. 2015; Gerke 2018). Low molecular mass organic acids (LMMOA) are a part of the carbon cycle and are also characterized as a labile, variable, and soluble component of SOM (Hubová et al. 2017). LMMOA, which is derived mainly from the root exudation, microbial activities, and the decomposition of SOM, plays vital roles in soil chemical, physical, and biological properties (Adeleke et al. 2017; Hubová et al. 2018; Xiao et al. 2010).

The stable part often called humic substances (HS) form roughly 80% of SOM and behave differently in the terrestrial ecosystem depending on the parent materials, vegetation types, climate conditions, land use, and topography (Ussiri et al. 2003; Senesi et al. 2003). Humic substances, however, significantly affect the chemical sorption, capacity of soil buffering, micronutrient availability, and level of trace elements toxicity and metal deficiency in the soil (Guimarães et al. 2013; Tang et al. 2014; Tunega et al. 2020). In the early concept, the HS structure was described as polymer systems containing various molecular weights, which are relatively similar to other natural biological macromolecules (e.g., lignin, proteins, and carbohydrates) (Yang et al. 2004; Debska et al. 2007). On the contrary, Piccolo (2002) reviewed that HS could be better described as a supramolecular association

than being constituted by macromolecular polymers, as the traditional concept believed. A new view of HS as supramolecular associations could be interpreted as relatively small humic and chemically diverse organic molecules linked together by hydrogen bonds and hydrophobic interaction (Sutton and Sposito 2005; Gerke 2018). On the other hand, Lehmann and Kleber (2015) reviewed and argued that the terminology of HS in soil science led to misinterpretations or varying definitions from researchers. Therefore, the HS in our study was interpreted according to Piccolo's review. For a similar reason, we used the description of 'alkaline extractable organic substances (AEOS) for a mixture or an association of compounds extractable with alkaline solutions. Especially it is important in surface horizons, where these compounds could not be present in the classical concept of humification processes. Extracts from L and F horizons contain a mixture of organic compounds such as lignin, carbohydrate, protein, lipid, and carbonyl due to the fresh and non-decayed materials.

The AEOS can be subdivided into low soluble (soluble only in alkaline nature and in mineral horizons, also called humic acids (HA)), soluble (soluble in whole pH scale and in mineral horizons, also called fulvic acids (FA)). Humic and fulvic acids have been ascribed as the main component of humic substances and have similar structures and compositions (Ribeiro et al. 2001). HA and FA are relatively important complexing ligands for most metal ions in the terrestrial ecosystem (Porcal et al. 2009) and are fascinating to researchers in their interaction and transformation in the humic substances (Zhou et al. 2014). HA and FA generally differ in functional groups and element content. HAs are typically larger associations and contain fewer oxygen-containing functional groups than FA (Tang et al. 2014; Canellas et al. 2008). The HA and FA behave and consist differently through the soil profile due to the decomposition rate, mobility, chemical sorption, origins and the degree of SOM maturity (Debska et al. 2007; Machado et al. 2020; Banach-Szott et al. 2021). Porcal et al. (2009) reviewed that the HA:FA ratio decreased through the soil profile in Podzolic soil. This could reflect the reduction of mobility and degradation of HA. Conversely, once it occurs in Cambic soil, the degradation and mobility of HA are double the values in A- and AB-horizon than in B-horizon. Ussiri et al. (2003) found that HA was less acidic compared to FA and contained more aliphatic and phenolic content than FA.

This study benefits from known study site history. Planted spruce monoculture is almost 100 years old and it replaced previously planted or naturally growing beech forest, which still occurs in vicinity. A comparison of the soil properties of these two stands thus brings information about the influence of spruce cultivation, i.e., the input of qualitatively different organic material, a different distribution of precipitation or perhaps even a different distribution of roots on soil conditions with detailed consideration of the qualitative parameters of SOM. Moreover,

89   there are few studies that address the qualitative changes of SOM within the entire soil profile including both

90   surface organic horizons and mineral horizons.

91   To fill this lacuna, this study aims: (1) to determine the various organic components through the entire forest soil

92   profile, (2) to evaluate the changes in chemical soil component and compositions (aliphatic, aromatic, and other

93   functional groups presence) of extracted AEOS in beech and spruce forest soil horizons using diffuse reflectance

94   infrared Fourier transform (DRIFT) spectroscopy, and (3) to evaluate effect of spruce planting on organic matter

95   compositions in whole soil profile. We hypothesized that the various organic compounds (AEOS, LMMOA, and

96   DOC), which derive from the acidic forest with contrasting vegetation covers, similar bedrock and soil types,

97   incorporate and transform differently through the forest soil profiles (e.g., from litter horizon to the subsurface

98   mineral horizons).

99   **Materials and methods**

100   *Study area and soil sampling*

101   The research was conducted in the Jizera Mountains in the northern part of the Czech Republic. The area was

102   adversely affected by atmospheric acid deposits during the 1980s-1990s due to the nearby coal-fired power station.

103   Number of previous studies were focused on these mountains (Borůvka et al. 2005; Drábek et al. 2007; Borůvka

104   et al. 2009; Pavlů et al. 2021). The study area is called Paličník (50.8683900N, 15.2527000E). The mean annual

105   precipitation and temperature are roughly 1200 mm and 4-7ºC, respectively. The study was carried out in specific

106   mono-forest species - European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* L. Karst.). The soil

107   types are characterized as Entic Podzols under spruce and Dystric Cambisol under beech forest; both are strongly

108   acidic (Tejnecký et al. 2013). However, the canopy closure of spruce (40%) is lesser than beech forest (87%). The

109   age of spruce and beech forest are roughly 100 and 180 years, respectively (Bradová et al. 2015).

110   Thirty soil samples were collected from different soil horizons (L: litter horizon, F: fermentation horizon; H:

111   humified horizons, A: organo-mineral horizon, B: subsurface mineral horizon (cambic horizon under beech, spodic

112   humusosesquioxidic horizon and cambic horizon enriched with iron oxides under spruce)). Three individual soil

113   pits (approximately 50×50 cm) were dug from each forest for soil description and sample collection. On the other

114   hand, each soil sample was thoroughly mixed and then divided into two parts. The first part was analyzed in a

115   "fresh" state, representing actual soil moisture and the second part was air-dried and passed through a 2 mm sieve.

116   The air-dried soil samples from L horizon were blended to get fine particles and sieved to 2 mm.

117

118 *Soil analysis*

119 The active pH (pH_{H2O}) was determined in a ratio 1:4 (soil:water, w:v) for organic horizons and 1:2 for mineral

120 horizons and measured using the pH-electrode SenTix 21 (Inolab pH level 21, WTW, Germany). The thermal

121 gradient with continuing heating up to 900°C and with a soliTOC cube (elementar, Lanenselbold, Germany) was

122 used for evaluation the stability and quality of SOM, according to Rennert and Herrmann (2022). The cation

123 exchange capacity (CEC) was determined in 0.1M $BaCl_2$ extract of the soil, which is according to the standard

124 ICP Forest methods (Cools and De Vos 2016). The SOC content was determined by rapid dichromate oxidation

125 techniques and in accordance with Tyurin's method (Sparks 1996). The dissolved organic carbon (DOC) and low

126 molecular mass organic acids (LMMOA) were determined with the fresh soil samples that were extracted by

127 deionized water (ratio: soil:water 1:10, w:v). The DOC was measured at 340 nm using a spectrophotometer after

128 dichromate oxidation, according to Tejnecký et al. (2014). The content of water-extractable LMMOA was done

129 using ion chromatography (IC) in conjunction with suppressed conductivity (capillary high-pressure ion

130 chromatography - HPIC). Dionex ICS 4000 and ICS 6000 (Thermo Scientific, USA) system equipped with Dionex

131 IonPac AS11-HC 4 µm (Thermo Scientific, USA) guard and analytical columns were used (Hubová et al. 2018).

132 Generally, all of the analytical procedures were secured from point of view of Quality Assurance and Quality

133 Control (QA and QC). The procedures ensuring laboratory QC and QA were done according to the standard

134 laboratory practices, including repeated measurements, processed blanks, fortified standards, spiked samples, and

135 mainly the use of the certified referential materials.

136 *Alkaline extractable organic substances*

137 Alkaline extractable organic substances (AEOS) were isolated from soil samples (L, F, H, A and B horizons) and

138 were determined according to the International Humic Substance Society (IHSS) fraction method, modified by

139 Piccolo et al. (2000). Sixty grams of soil was extracted by adding 300 ml of a mixture of 0.5M NaOH and 0.1M

140 $Na_4P_2O_7$ and then shaken for 24 h. Dissolved AEOS was separated by centrifugation at 4000 rpm for 15 min and

141 then transferred into beakers. This extraction was repeated three times. The solution was acidified to pH 1.0 using

142 HCl and left overnight in the refrigerator for precipitation and separation of AEOS into low soluble (insoluble in

143 acid nature) and soluble (soluble in whole pH scale), which are finally separated by centrifugation. Low soluble

144 AEOS was redissolved with 1M NaOH and reprecipitated with HCl. To purify the co-extracted clay, the precipitate

145 they were shaken with 300 ml of mixture solution of 0.5% HCl and 0.5% HF (v/v) for two days. The suspension

146 was centrifuged at 4000 rpm for 10 min and neutralized. They were then transferred into a dialysis bag and soaked

147 with distilled water in a cylinder to free chlorine. Finally, they were frozen and freeze-dried. The soluble AEOS

148 was purified using the hydrophobic resin in the column. A 0.5M NaOH solution was used to release the soluble

149 AEOS sorbed in the resin. Finally, they were neutralized, then dialyzed, frozen and freeze-dried.

150 *Diffuse Reflectance Infrared Fourier Transform Spectroscopy*

151 The freeze-dried powders of AEOS were measured using an infrared spectrometer (Nicolet IS10) and OMNIC

152 9.2.41 software (Thermo Fisher Scientific Inc., USA). The samples were recorded by 120 scans and wavenumbers

153 ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} using the gold mirror as the background. The unit of the

154 reflectance was converted to Kubelka-Munk. However, to determine relative changes of the reflectance bands in

155 DRIFT spectra and for spectra comparison in percentage, the relative reflectance (rR) of the selected band was

156 calculated by dividing the sum of all selected bands heights (2929, 1724, 1633, 1517, 1447, 1403, 1280, and 1045

157 cm^{-1}) and multiply it by 100 (e.g., rR$_{1724}$ = R$_{1724}$/$\sum$R$_{(2929-1050)}$*100) (Haberhauer and Gerzabek 1999; López et al.

158 2008).

159 *Statistical analysis*

160 Mean comparisons of the chemical compositions among the soil horizons under beech and spruce were statistically

161 analyzed using analysis of variance (ANOVA) at an error level of 0.05 (confidence level of 95%). *T* test was also

162 performed for comparison the chemical compositions and chemical soil structures between beech and spruce

163 stands using IBM SPSS (version 29, New York, USA) software. The statistical differences between horizons and

164 vegetation covers were presented in letters (a, b, c, and d) using the Tukey test.

165 **Results and discussion**

166 *Basic soil characteristics*

167 The distribution of pH values within the soil profile was similar for both stands (figure 1). From the soil surface

168 (L horizon), the pH gradually decreased to horizon A and then rose again to B horizon. While in the mineral

169 horizons A and B the values in both stands were similar, in the surface organic horizons the acidifying influence

170 of the spruce forest, respectively the litter, was evident. This difference was also demonstrated at the studied site

171 in previous researches working with longer time series of sampling and larger sets of samples (Tejnecký et al.

172 2013, Burešová et al. 2021). However, the distribution of the cation exchange capacity (CEC) was also alike

173 tendency within the soil profiles under both forest species. The CEC decreased significantly from L to B horizons,

174 ranging from 51.9 ± 2.2 to 7.2 ± 2.2 cmol+kg^{-1} under beech and from 29.7 ± 2.7 to 7.0 ± 1.6 cmol+kg^{-1} under spruce

175 (Table S1). It was similar to the tendency of soil organic carbon content (SOC), which had been stored more in

176 the uppermost layer than in the deeper soil horizons (L > F > H > A > B) under both stands. When compared

177   between both forest species, it showed higher CEC in beech stands than spruce one (Table S1). Generally, the

178   CEC increases with increasing SOC (Cremer and Prietzel 2017) and further discussion was in Thai et al. (2023).

179   The decrease in pH and CEC after the change of the natural beech stand to a spruce monoculture can subsequently

180   lead to leaching of nutrients (Berthrong et al., 2009; Gruba and Mulder, 2015) and an increase in the content of

181   some potentially toxic elements (Al and Mn) not only in the soil environment (Augusto et al. 2002, De Schrijver

182   et al. 2007), but also in surface water (Kopáček et al., 2009). This is relatively well-studied in areas previously

183   affected by anthropogenic acidification (Kopáček, Veselý 2005, Pavlů et al., 2018, 2021), but similar problems

184   can arise in areas with large-scale cultivation of conifer plantations in place of original broad-leaved forests e.g.,

185   in developing countries (Fagan et al. 2022, Salas et al., 2016).

186   The thermal gradient with continue heating, we evaluated at least two maxima of the temperature (Tmax, Tmax2)

187   depending on CO_2 evolution (figure S1). Under beech forest, the position and temperature of the first Tmax showed

188   Tmax $\geq$ 400°C and the second local maxima (Tmax2) was Tmax2 $\geq$ 500°C (figure 1). A significant difference

189   under beech forest was observed through the whole soil profile (L >F >H< A< B). Under the spruce stands, it

190   showed that the values of Tmax and Tmax2 were similar to the values found in beech forest (Tmax $\geq$ 400°C and

191   Tmax2 $\geq$ 500°C) and no significant difference was observed between forest stands in most of the horizons except

192   for L horizon, where in the spruce was higher values than in beech stands. The distribution of the Tmax values

193   within the soil profile under spruce gradually decreased from L to H horizon and then rose again from A to B-

194   horizons, while the Tmax2 was decreased with increase depth (L >F >H, A, B). Generally, the Tmax ranging from

195   300-350°C indicated the dominance of labile SOM and lack of interaction with minerals, while the Tmax ranging

196   from 350-400°C indicated the loss of aromatic compounds such as lignin and other polyphenols and high

197   recalcitrant organic matter (Fernández et al. 2011; Barreto et al. 2021a). Nonetheless, the Tmax greater than 400°C

198   indicated the highly recalcitrant materials rich in aromatic components (Barreto et al. 2021b) and revealed stability

199   of SOM in the soil profile or the presence of black carbon (Fernández et al. 2011). The increase Tmax values from

200   H to B horizon under both forest stands demonstrated the chemically interacted with the mineral surface (Rennert

201   and Herrmann 2022).

202   ***Dissolved organic carbon and low molecular mass organic acids***

203   The dissolved organic carbon (DOC) was more abundant in the F and H horizons than in L, A and B horizons

204   under both forest stands (figure 1). Under beech, the LMMOA content followed the order L, F > H > A > B

205   horizons, while under spruce the highest concentration of LMMOA was observed in F and H horizons (figure 2).

206 The most frequent LMMOA under both forest species were citrate, lactate, oxalate and quinate, which were all

207 mostly observed in the organic horizons (L, F and H). This indicates that there was greater litter, root materials,

208 and biological activity occurring in the organic horizon, which led to an increased rate of SOM decomposition and

209 both directly and indirectly increased LMMOA production (Hubová et al. 2018). The release of a wide range of

210 organic acids that were produced by microorganisms was observed by Adeleke et al. (2017) during the

211 decomposition of forest litter. Other reasons for the increased concentration of LMMOA in the upper horizons can

212 be attributed to soil acidity and plant root exudates (Berg and McClaugherty 2008; Thai et al. 2021).

213 Under beech forests, when compared to spruce forests, higher content of DOC was found in the L, F and H horizons

214 (figure 1), while LMMOA concentration (almost the organic acids, except for quinate) were higher in L and F

215 horizons (figure 2). The lower content of DOC and LMMOA in the organic horizon of spruce forests than beech

216 forests (Table S2) indicated that there was more recalcitrant residues (slowly decomposable). With that being said,

217 the higher biological activity and decomposable litter under beech than under spruce forest, which observed in

218 locality by Buresova et al. (2021), produced more organic acids. Interestingly, despite lower concentration in the

219 surface horizons of the spruce forest, quinate, lactate, formate, and oxalate, as well as DOC and SOC were higher

220 in the A horizon, in comparison to the beech forest (Table S1, S2). The results indicated that the podsolization

221 process and the association among SOC, DOC, and LMMOA, where SOC concentrations positively correlated to

222 LMMOA and DOC. A positive correlation between SOC and LMMOA ($p < 0.01$, $r = 0.45*$) and between DOC

223 and LMMOA ($p < 0.001$, $r = 0.55**$). Podzolization is a long-term natural process conditioned by low soil pH and

224 base saturation. The formation of well-differenced soil profile represents approximately 300–3000 years

225 depending on climate conditions (Sauer et al., 2007). Chemical changes conditioned for example by vegetation

226 cover change are faster (Lundström et al. 2000; Dlouhá et al. 2009). The formation and downward transport of

227 organic acid complexes with Al and Fe is one of the processes that have been proposed to explain podzol formation,

228 and the quality and mobility of SOM play an important role in it. (Lundsröm et al. 2000).

229 ***The spectroscopic characterization of alkaline extractable organic substances***

230 The DRIFT spectra of alkaline extractable organic substances (AEOS) extracted from the soil profile under beech

231 and spruce forests are shown in figure 3 and figure 4. The major reflectance bands of soluble AEOS spectra under

232 both forest species are in the region at 3400-3300 cm^{-1} (H-bonded OH groups), 2950-2800 cm^{-1} (aliphatic C-H

233 stretching), 1724 cm^{-1} (C=O stretching of COOH and ketones), 1633 cm^{-1} (C=O stretching of amide I, quinone,

234 H-bonded conjugated ketones), 1517 cm^{-1} (N-H bending and C=N stretching), 1477 cm^{-1} (OH deformation and C-

235   H stretching of phenolic OH), 1403 cm^{-1} (OH deformation of CH$_2$ and CH$_3$), 1280 cm^{-1} (C-O stretching and OH

236   deformation of COOH), and 1045 cm^{-1} (polysaccharides).

237

238   In general, the soluble and low soluble AEOS spectra were clearly distinguished in each soil horizon for both

239   forest species. In the soluble AEOS spectra, it was observed that more peaks were visible in L, A, and B horizons

240   than in F and H horizons. The soluble AEOS spectra under both forest species showed that the peak of aliphatic

241   C-H stretching was less visible with increasing depth. This indicated the preferential biological degradation of

242   carbohydrates, which are the main parts of the O-Alky C fraction (López et al. 2008). However, the band at 1724

243   cm^{-1}, which is ascribed to carboxylic groups, was clearly seen in A horizon comparing the L, F, H, and B horizons

244   under beech, whereas in spruce, the band at 1724 cm^{-1} was clearer in the A and B horizons than in the L, F and H

245   horizons (figure 3). Interestingly, the band at 1724 cm^{-1} in B horizon under spruce had the same height of peak as

246   the peak of the shoulder reflectance band at 1633 cm^{-1}. This indicated that the C=O stretch of COOH and ketones

247   were present in deeper soil profiles and resulted from the oxidative cleavage of lignin side-chain and aromatic

248   rings during the degradation (López et al. 2008). A higher abundance of DOC in F and H horizons (figure 1) was

249   an indicator of carboxylic groups becoming more soluble and transport into deeper soil horizons. It was noticed

250   that there were opposite intensities of bands (1633 ≥ 1280 cm^{-1}) in most of the soil horizons, except for F horizon

251   (1633 ≤ 1280 cm^{-1}) under both forest species. This result could be due to the initiated decomposition of OM and

252   more abundant organic acids; therefore, it promoted more OH deformation of COOH in F horizon. On the other

253   hand, it suggested that increasing the degree of decomposition and maturity of OM enhanced higher aromatic

254   components in the deeper soil horizons (H, A, and B horizons) (Margenot et al. 2015; Veum et al. 2014). The band

255   at 1517 cm^{-1} representing N-H bending and C=N stretching was more intense in the L horizon, followed by F, H,

256   A, and B horizons. A similar result was also found by Leinweber et al. (2001). The band at 1447 cm^{-1} and 1403

257   cm^{-1} were more intense through the soil horizons (figure 3). This revealed the presence of lignin structures at the

258   amplitude, and thus eliminating the amplitude of the band at 1447 cm^{-1} and exposing organic compounds,

259   increasing decomposition, and humification rate could cause peaks to be lower for some soil horizons (L and F

260   horizons) (Machado et al. 2020). However, the disappearance of the polysaccharide chains through the soil profiles

261   (figure 3) signified that the polysaccharides had been used or decomposed by soil microorganisms (Leinweber et

262   al. 2001).

263

264   The major bands of low soluble AEOS are at 3400-3300, 2950-2800, 1724, 1633, 1517, 1403, 1280, and 1045 cm$^-$

265   ^{1}. The number of peaks in low soluble AEOS spectra was clearly visible in the L, F, and H horizons compared to

266   A and B horizons under both forest species (figure 3). The peaks at aliphatic groups (2950-2800 cm^{-1}) relatively

267   increased with increasing depth under beech forests, while the peaks under spruce had higher intensity in A horizon

268   (figure 3 and figure 4). This result could be explained by the fact that the amount of aliphatic groups within low

269   soluble AEOS increased during decomposition and the formation of the micelles of low soluble AEOS (Sierra et

270   al. 2005). The bands of C=O stretching of COOH and ketones (1724 cm^{-1}) were clearly visible in intensity with

271   increasing depths under both forest species. The aromatic C=C stretching (1633 cm^{-1}) increased with depth under

272   beech, while spruce stands were relatively constant through the soil horizons. These results showed similarity to

273   the findings of Tatzber et al. (2007). Interestingly, the peaks between 1724 and 1633 cm^{-1} showed that the peak at

274   1724 cm^{-1} is lower (1724 < 1633 cm^{-1}) in F, A, and B horizons, while in the H horizon had similar height of

275   intensity under the beech forests. In the spruce forests, the peak at 1724 cm^{-1} is similar in height to the shoulder

276   peaks at 1633 cm^{-1} in L and F horizons, but it had higher intensity (1724 > 1633 cm^{-1}) in H, A, and B horizons.

277   The higher 1724 cm^{-1} than 1633 cm^{-1} in the subsoil horizon was due to the ester formation and elimination of the

278   stretching mode of COO$^-$ ions (Stevenson 1994). Additionally, this phenomenon explained that the 1724 cm^{-1} band

279   became progressively weaker with an increase in color intensity, indicating a progressive decrease in COOH

280   content with increasing molecular weight. These systematic changes occurred in the intensities and positions of

281   bands in 1660-1600 cm^{-1} regions (Stevenson 1994). Besides that, these results revealed that the structures of

282   organic matter were more stable under beech than spruce (Pavlů and Mühlhanselová 2017). The gradual

283   disappearance of N-H bending and C=N stretching (1517 cm^{-1}) with depth under both forest stands (figure 3) were

284   interpreted that the N being decomposed by soil microorganisms and could result from degradation of various

285   moieties of forest litter substances from L to B horizons (Haberhauer et al. 1998). It was also noticed that the peak

286   of N-H bending and C=N stretching in the beech forests was higher in L and F horizons than in the spruce one

287   (Table S3a, S3b). The results agreed with Mládková et al. (2006) that low soluble AEOS originating from the

288   organic horizons under beech forests were relatively richer in nitrogen functional groups than substances

289   originating from spruce stands. The band of the OH deformation and C-H stretching of phenolic OH were clearly

290   visible in all horizons under both forests. The band at 1280 cm^{-1}, which is ascribed to C-O stretching and OH

291   deformation of COOH, was lower in deeper soil depths. This pointed to the higher maturity of low soluble AEOS

292   in the uppermost soil layer (Pavlů and Mühlhanselová 2017). It showed a similar tendency of the polysaccharides

293   bands, which were lower intensities with deeper soil horizons. However, it was observed that the band at 1280 cm$^-$

294   ^{1} was higher than the other neighboring peaks, such as 1447, 1403, and 1280 cm^{-1}, in most of the soil horizons

295   under spruce, while in beech forests it was observed only in F horizon and lower peaks with depth.

296   To compare the spectra of AEOS, the soluble AEOS spectra had three main dominant peaks (1633, 1403, and 1280

297   cm^{-1}), while low soluble AEOS spectra had more well-separated peaks (2950-2800, 1724, 1517, 1403, and 1280

298   cm^{-1}). Generally, the soluble AEOS was readily affected by the degree of humification and easily translocated in

299   the soil solution through the soil profile, while low soluble AEOS can indicate impurities associated with minerals

300   or water, or had a complexity of the chains and contained highly humification of organic compounds that were

301   insusceptible to degradation; and thus, tended to persist for longer (Ohno et al. 2009; Machado et al. 2020).

302   However, there was a higher saturation degree of low soluble than soluble AEOS, which was confirmed by the

303   reflectance bands between 2932 and 2853 cm^{-1}. The low soluble AEOS spectra appeared in two peaks (2932 and

304   2853 cm^{-1}) at the aliphatic C-H stretching group region in each horizon, while soluble AEOS spectra appeared in

305   only one peak and had lower intensities than low soluble AEOS under both forest stands. This result showed a

306   similar finding of Giovanela et al. (2004), and it attributed to the asymmetrical and symmetrical stretching of

307   methylene (-CH$_2$-) groups in low soluble AEOS and asymmetrical C-H stretching of methyl (-CH$_3$-) groups in

308   soluble AEOS. Remarkably, the intensity peaks of low soluble AEOS in the region of the C=O stretch of COOH

309   and ketones were more intense and clearly visible compared to high soluble AEOS spectra in most soil horizons.

310   The band at 1633 cm^{-1} appeared similar in height and was clearly visible under both AEOS spectra. The higher

311   intensity peaks of N-H bending and C=N stretching (1517 cm^{-1}) in low soluble than soluble AEOS spectra under

312   both forest tree species could be due to less labile structure in low soluble AEOS and exposure to the enzymatic

313   attack leading to increased humification; therefore, more molecular structures can be seen (Pospíšilová et al. 2015).

314   The percentage of N generally was higher in the low soluble AEOS, which reflected the presence of protein or

315   peptide fragments (Gaffney et al. 1996; López et al. 2008). It was consistent with the finding of Ussiri and Johnson

316   (2003) that low soluble AEOS maintained a higher proportion of N than soil organic matter, while soluble AEOS

317   was depleted in N. Another difference between the AEOS spectra was that the intensity peaks at 1403 cm^{-1} were

318   clearly seen and more intense in soluble compared to low soluble under both forest species. The band of the C-O

319   stretching and OH deformation of COOH observed in 1280 cm^{-1} were sharper and had higher intensity in soluble

320   than low soluble AEOS spectra. The peaks of polysaccharides at 1045 cm^{-1} were more visible under low soluble

321   AEOS in most of the soil horizons. In this case, it could be due to the lower stability of soluble AEOS. Therefore,

322   it showed the low incidence in the region of polysaccharides and possibly due to the aluminosilicate impurities

323   (Si-O stretch) (Madejova and Komadel 2001; Thai et al. 2021). However, ascribing these bands to aluminosilicate

324 impurities depended on some factors, including the additional presence of bands at 980 cm^{-1} (AlAlOH stretch) and

325 530 cm^{-1} (Al-O-Si stretch) (Machado et al. 2020).

326 It is presumed that the SOM, which consists of mainly humus substances, behaves differently through the beech

327 and spruce forest soil profile. In our results, the SOM has been stabilized under beech and spruce forests by

328 changing from available or reactive substances to more stable forms in forest soil profiles (beech and spruce), as

329 we observed the increases of aliphatic and carboxylic groups within low soluble AOES in deeper soil horizons and

330 the relatively increase of aromatic groups under beech stands. Additionally, it was also confirmed by the thermal

331 analysis, which showed Tmax values ranged between 400 to 500°C (figure 1). After clear-cutting forests for spruce

332 plantation in order to investigate soil development for a century, the content of SOM was rapidly reduced and lost

333 in the uppermost layers due to the humification process and organic matter decomposition for the first few years

334 and then started to stabilize the SOM with time (Jamroz and Jerzykiewicz 2022). It was noticed that the SOM

335 structures such as aliphatic groups, which were evaluated using DRIFT, were more frequent in the A horizon under

336 spruce and content of carboxylic groups increased in deeper soil horizons. It is consistent with the previous

337 research (Thai et al. 2023) that the SOC was increased in values in each horizon under beech, while under spruce

338 it was found only in A horizon after long-term observation from 2008 to 2020. This could explain that the SOC

339 under spruce increased after plantation, but decreased in 2015 due to the dry climate condition, which directly

340 affected SOC in the organic horizon (L, F, and H horizons). Our study also found that some organic acids were

341 found more in A horizon under spruce, indicating the soil development and formation of podsolization by starting

342 to release the Al and Fe from the A horizon to B horizons or deeper horizons (Lundström et al. 2000). In the beech

343 forests, on the other hand, the SOM structure like aliphatic bands relatively increased with deeper forest soil

344 horizons compared to spruce. This could result from the age of forest tree species, the canopy closure, and the

345 organic matter input. However, climatic conditions could alter the microbial activities and low molecular weight

346 fractions to be more depolymerized by products under spruce and could be easily lost and transported into deeper

347 soil horizons or leach into the groundwater (Lal 2008; Jamroz and Jerzykiewicz 2022; Zosso et al. 2023).

348 **Summary and Conclusions**

349 The study agreed with the hypotheses that the change in vegetation cover caused changes not only in basic soil

350 conditions, but also in the qualitative composition of soil organic matter. It can also be stated that the various

351 organic components were translocated differently through the forest soil profile. The content of DOC was high in

352 the F and H horizon under both forest tree species. The higher content of LMMOA, on the other hand, was found

353 in the L and F horizons under beech, and F and H under spruce. Compared both forest stands, in the beech forest

354   soil had higher DOC concentration in the organic horizons and higher abundance of LMMOA than in spruce forest

355   soil. The spectroscopic characterization of AEOS differs between organic and mineral horizons under both forests.

356   The most obvious difference was that the aliphatic groups in soluble AEOS spectra disappeared in deeper soil

357   horizons under both forest species. Contrary, the aliphatic groups in low soluble AEOS spectra are intense in A

358   horizon in spruce and their intensity relatively increased with depth in beech stands. This indicates the maturity of

359   organic matter in beech forests and the formation of micelles of low soluble AEOS. However, the results also show

360   some negative consequences of vegetation change specifically on the border of organic and mineral horizons. A

361   higher proportion of mobile components of SOM and acidic COOH groups in the spruce stand compared to the

362   beech stand, together with a generally lower pH and CEC in spruce forest soil, can lead to the leaching of nutrients,

363   to the release of risk elements into the soil solution, and to the acceleration of the podzolization process. On a

364   broader scale, the shift towards fast-growing coniferous plantations has relevant consequences on fundamental soil

365   functions and services such as biogeochemical nutrient cycling, including mentioned changes in exchangeable

366   cations and differences in organic matter composition, and carbon and nutrient stocks. Given that natural temperate

367   broadleaf stands are among highly threatened ecosystems requiring effective protection (the studied locality is part

368   of a protected area included in the UNESCO World Heritage List), it is important to understand the conversion to

369   cultural conifer stands as inappropriate.

375   **Supplemental Materials**

376   The datasets used and analyzed during the study are available from the corresponding author on reasonable request.

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683   **Figures and Tables**

684   **Figure 1**

685   The distribution of basic soil characteristics in litter horizon (L), fermentation horizon (F), humified horizon (H),

686   organo-mineral horizon (A), and subsurface mineral horizon (B – spodic or cambic) of the soil profile dug under

687   beech and spruce at Jizera Mountains (Czech Republic). (n = 3; mean; standard deviation). Cation exchange

688   capacity (CEC - cmol+kg[-1]), soil organic carbon (SOC - %), and dissolved organic carbon (DOC - mg kg^{-1}),

689   maxima temperature (Tmax and Tmax2 - °C).
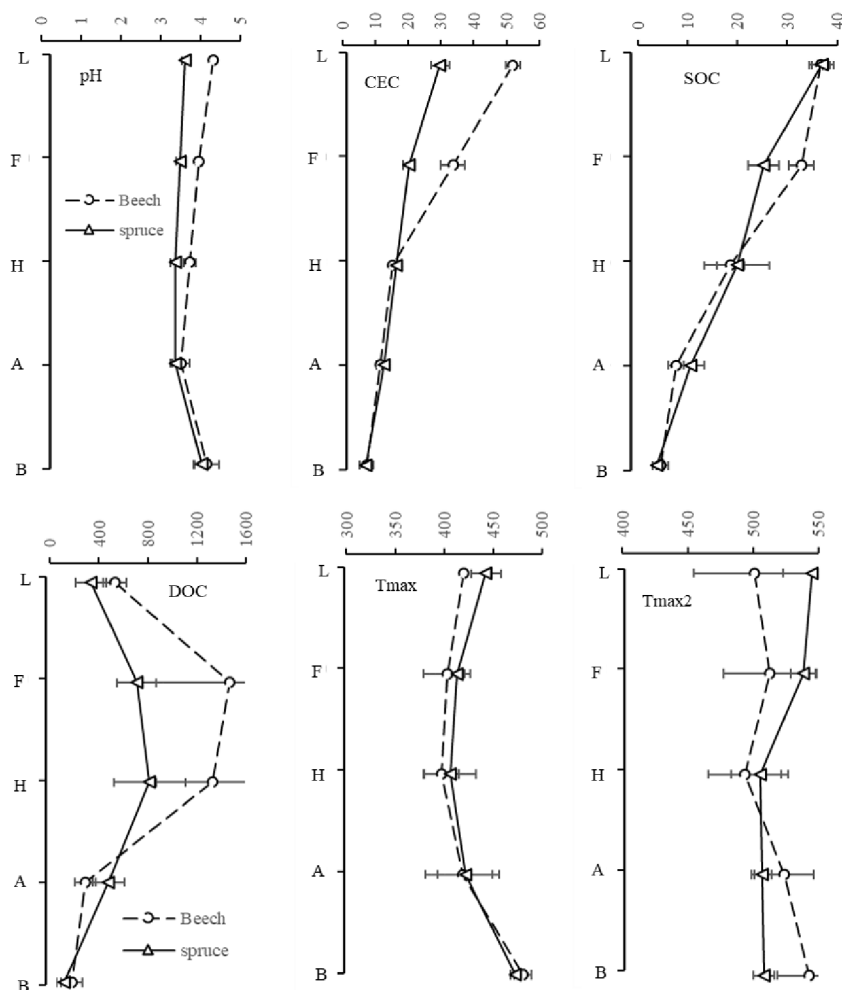
711 **Figure 2**

712 The concentration of low molecular mass organic acid under beech and spruce forest: A) comparing the low

713 molecular mass organic acids between beech and spruce forest expressed as mmol kg^{-1}; B) showing the

714 translocation of low molecular mass organic acids expressed as percentage (%) through the whole soil profile in

715 each forest stand, (mean value, n = 3). Litter horizon (L), fermentation horizon (F), humified horizon (H), organo-

716 mineral horizon (A), and subsurface mineral horizon (B – spodic or cambic).
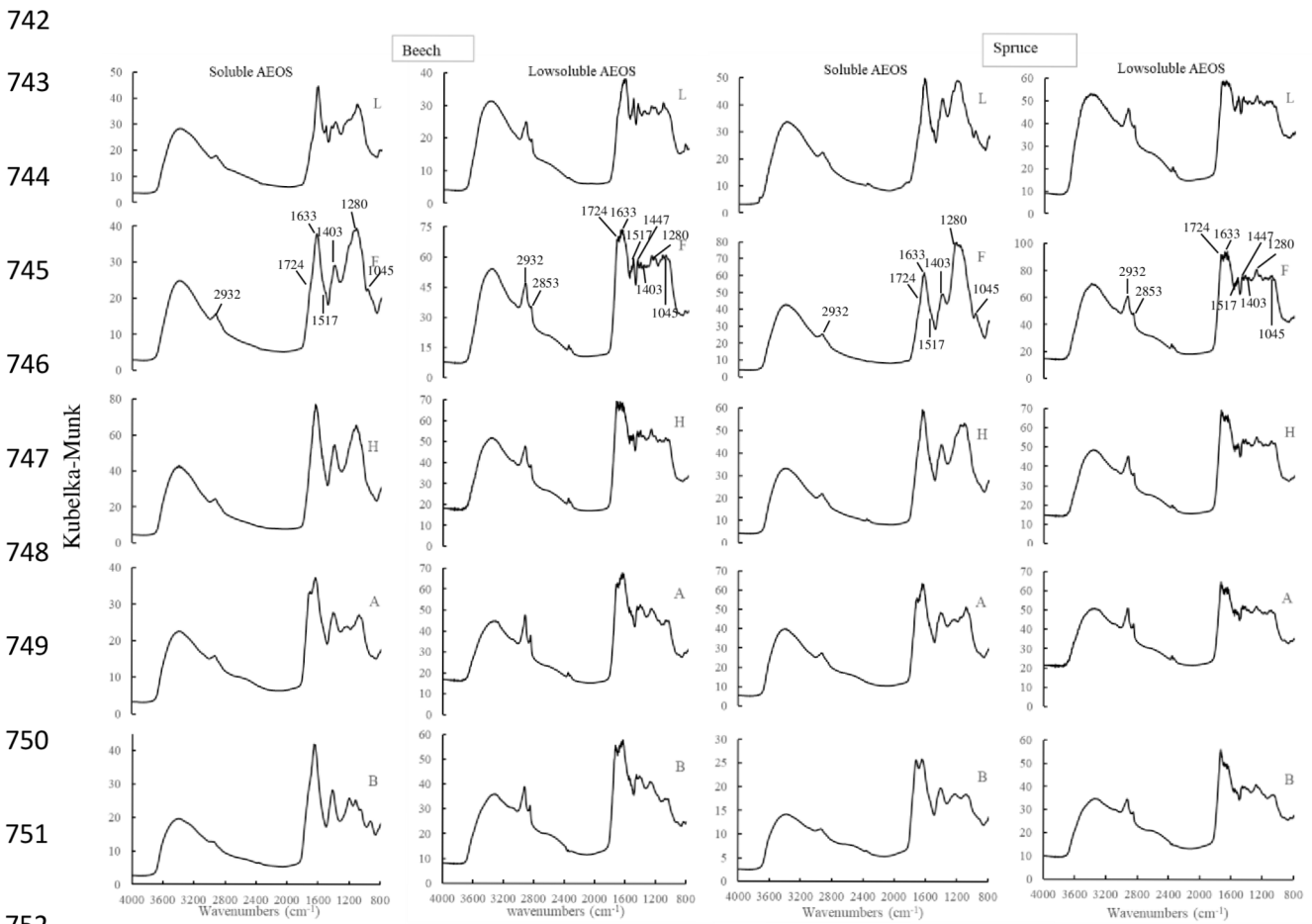
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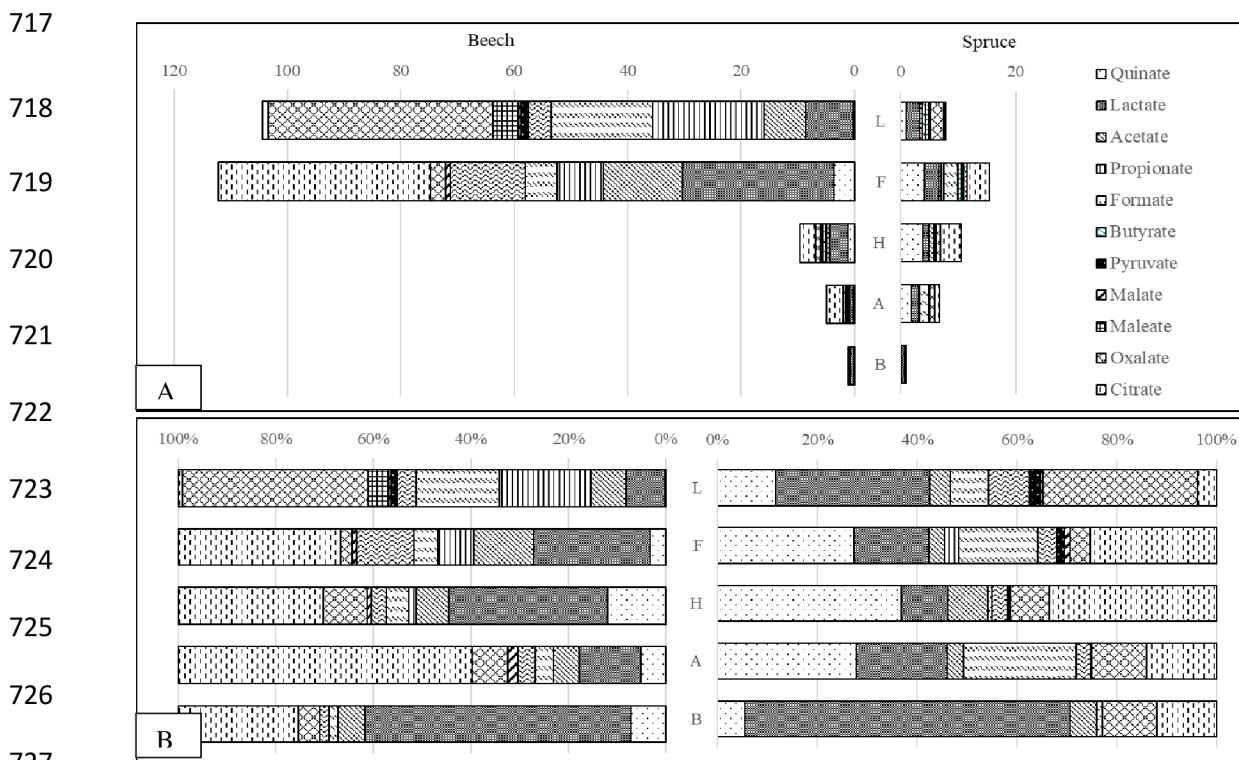
Figure 3

The spectra of soluble and low soluble alkaline extractable organic substances in each horizon under beech and spruce forests (mean spectra from three individual samples). Litter horizon (L), fermentation horizon (F), humified horizon (H), organo-mineral horizon (A), and subsurface mineral horizon (B – spodic or cambic).

Figure 4.

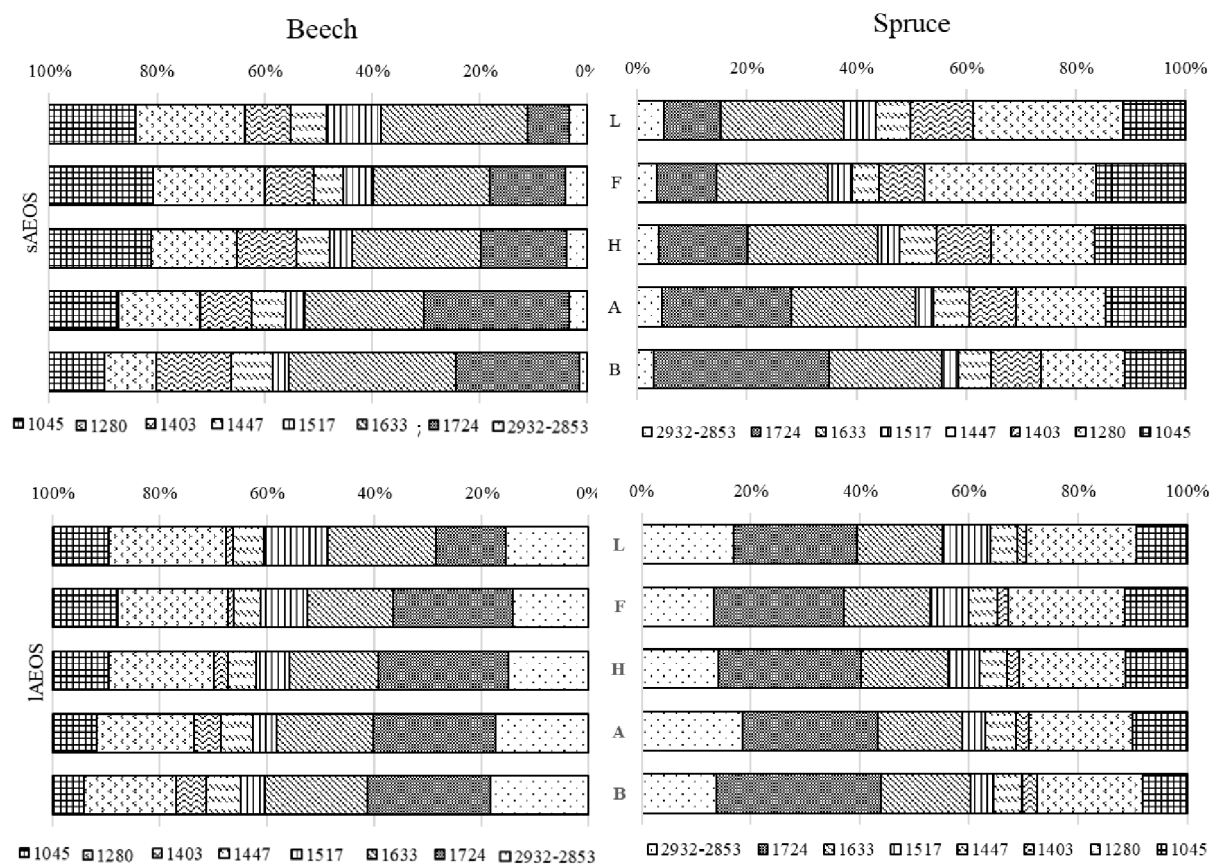The reflectance band of soluble alkaline extractable organic substances (sAEOS) and low soluble alkaline

extractable organic substances (lAEOS) expressed as % in each horizon under beech and spruce forests (mean

value, n = 3). Litter horizon (L), fermentation horizon (F), humified horizon (H), organo-mineral horizon (A), and

subsurface mineral horizon (B – spodic or cambic).

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